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Example on the Use of Operando Spectroscopy for Developing Mechanistic Insights into Industrial Catalysts and Catalytic Processes

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Abstract: In this contribution, we present an industrial example on how tailored operando spectroscopic methodologies provide the insights needed for the development of new catalytic technologies and support their global utilization. We describe the use of operando spectroscopic methods to investigate how the CO oxidation performance of catalysts is impacted by NO_x, H₂, temperature, and moisture, as well as the catalyst support. This operando spectroscopic analysis provides mechanistic insights into the current diesel oxidation catalyst (DOC) system and shines light on the material and process development efforts on future DOC catalysts for low-temperature emission control to meet the new regulations. This investigation has shown that at cold-start temperatures, the nitrate growth can occupy the precious metal–alumina support interfacial sites that are critical for O₂ dissociation and/or oxygen transfer and hinder CO conversion. Introduction of hydrogen on the catalyst surface can inhibit the nitrate growth, which in turn keeps these critical interfacial sites open.

Keywords: operando spectroscopy; heterogeneous catalysts; DRIFTS; CO oxidation; DOC



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1. Introduction

The development of novel catalysts is necessary to support the sustainable progress of our industrialized society. Characterization efforts provide critical information on catalytic technologies and help develop a mechanistic understanding to support further advancements in their industrial application. Operando/in-situ spectroscopy is a powerful material characterization tool in the field of catalysis, which conducts spectroscopic characterization under catalytic working conditions. Consequently, the material structural information can be correlated with catalytic activity and selectivity. Ultimately, fundamental reaction mechanisms can be revealed based on operando spectroscopy analysis. The material characterization is usually carried out by one of the following spectroscopy methodologies: Fourier-transformed infrared (FT-IR) [1], ultraviolet–visible (UV-Vis) [2], Raman [3], nuclear magnetic resonance (NMR) [4], and X-ray spectroscopy methods involving diffraction, adsorption, and scattering [5–7]. The catalytic activities are measured by Mass Spectrometers or FT-IR Gas Analyzers. By utilizing these methods and others, operando spectroscopy plays a significant role in the electro-catalysis, heterogeneous catalysis, photocatalysis, and battery fields [8–12].

The structural identification of reactants, intermediates, and products is a critical aspect of the development of new and improved industrial catalytic processes. It is even more insightful when it includes the study of surface adsorbates at catalytic working conditions. The variation of surface adsorbates as conditions change (e.g., temperature and gas feed composition) can be correlated to the changes in material properties and catalytic performance under these reaction conditions. Another piece of structural identification is about the solid structures that constitute the catalyst architecture, as it dictates key performance attributes such as accessibility, stability, and regenerability. Information from

both aspects can be identified by operando/in-situ spectroscopy, which shines light on the catalytic material development and identification, as well as the mechanistic understanding. In this contribution, we will present an example of using operando diffuse reflective infrared Fourier transform spectroscopy (DRIFTS) for the structural characterization of catalysts and the development of mechanisms for catalytic applications in the field of environmental catalysis.

The diesel oxidation catalyst (DOC) is one of the key parts of the catalytic converter used in diesel engine after-treatment systems. The DOC works under lean conditions with an excess of air-to-fuel ratio compared with the stoichiometric mixture in gasoline engines. The major function of the DOC is the oxidation of CO and hydrocarbons (HC) in the diesel engine exhaust. The NO in the exhaust can also be oxidized to NO₂ when passing through the DOC. The typical DOC materials include alumina-supported platinum group metals (PGMs) with hydrocarbon traps [13]. A common issue with supported PGM catalysts at low temperatures is the CO poisoning—the strongly bonded CO on the PGM surface limits the O₂ access for oxidation, which can be usually overcome by raising the temperature [14]. In order to improve the DOC activity at low temperatures, researchers introduced hydrogen pulses on DOC catalysts during the cold start of diesel engines, which significantly increased the CO conversion at low temperatures [15–21].

Possible mechanisms for the improved CO conversion by hydrogen pulsing include, but are not limited to: (1) the competitive adsorption between CO molecules and hydrogen on PGM surfaces; (2) more active sites being generated by H₂ reduction on PGM; (3) a more active O atom generated via NO_x reduction by H₂; and (4) release of active sites taken by nitrates due to nitrate decomposition by H₂ reduction. In this study, a mechanistic investigation of hydrogen pulsing's impact on DOC performance by operando spectroscopy was conducted on an alumina-supported Pt catalyst. Spectroscopic evidence on working catalysts provide insights into improved CO oxidation activities due to the release of PGM-support interfacial sites under H₂ pulsing at the cold start of diesel engines.

2. Results and Discussion

In order to decouple various contributing factors, a simple system of CO oxidation without NO_x in the gas feed was first examined for the hydrogen impact. In this set of experiments, interesting questions about molecular interaction processes to be considered include: (1) whether the hydride on the PGM surface can be formed and how CO adsorption will be impacted by H₂ (competitive adsorption between hydride and CO); (2) how does the PGM surface change under H₂ impact; (3) whether there is an impact on CO conversion from H₂; and (4) what is the rate-limiting step, as well as other points that could support a deeper mechanistic understanding. To investigate the H₂ and CO interaction on the PGM surface, CO DRIFTS experiments on a dehydrated and reduced fresh Pt/Alumina sample were conducted. Figure 1 shows the DRIFTS data for CO desorption (pre-adsorbed CO by flowing 70 mL/min of 1% CO/Ar for 30 min) at three temperatures in two environments—Argon vs 2.4% H₂/Ar. In Figure 1, the solid lines represent the desorption in Argon, while the dashed lines represent the desorption in 2.4% H₂/Ar. The peak at 2060–2070 cm^{−1} and the shoulder at 2082–2086 cm^{−1} can be assigned to the CO linearly adsorbed on the metallic Pt and Pd sites, respectively [22,23]. The wide and weak features at 1950–1990 cm^{−1} are due to the CO being bridge-adsorbed on two PGM atoms [24]. A broad peak at ~1820 cm^{−1} can be assigned to the CO adsorbed on three PGM atoms, which is an indication of a large PGM particle formation [25]. Figure 1 clearly shows that the pre-adsorbed CO on the linear adsorption sites can be completely desorbed in Argon within 20 min, while only a slight decrease was observed for the desorption in H₂. The stronger CO adsorption on the reduced sample is likely due to the more available metallic Pt⁰ and Pd⁰ surface upon reduction. The peak intensity on the double- and triple-bridged CO adsorption sites was barely changed within 20 min for both desorption environments. Therefore, the introduction of H₂ does not remove CO from the PGM surface, suggesting that the CO adsorption on the PGM surface is stronger than hydride bonding (if any). As a first

step in this mechanistic investigation, this CO DRIFTS experiment confirms that there is no/negligible competitive adsorption between CO and H₂ on the PGM surface.

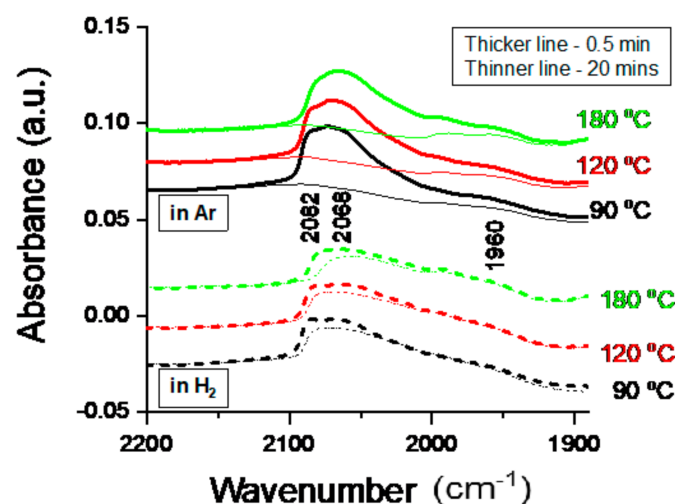


Figure 1. IR results of a diesel oxidation catalyst (DOC) catalyst sample for CO desorption in Ar compared with 2.4% H₂/Ar at 90, 120, and 180 °C (pre-adsorbed with CO (1%) balanced in Ar for 30 min before each desorption).

To address questions 2–4 of this mechanistic investigation, CO oxidation reactions were conducted to examine the hydrogen impact. Figure 2 shows the CO adsorbed on the PGM surface during the oxidation reactions at different temperatures on an aged Pt/Alumina sample. Under the presence of hydrogen, the PGM surface is reduced with a significantly increased peak at 2067 cm^{−1} for CO–Pt⁰ at 90 and 120 °C. Correspondingly, about a 10–15% higher CO conversion was achieved at lower temperatures in the activity results shown in Figure 3a. This result suggests that at low temperatures, there is a PGM surface reduction upon hydrogen exposure, which slightly increases the CO oxidation efficiency. Additionally, analysis of the water content detected in the Mass Spectrometer in Figure 3b indicates that at 90 and 120 °C the reaction 2H₂ + O₂ = 2H₂O is not activated. At 180 °C, the aged Pt/Alumina catalyst is so active that it reaches a 100% conversion with or without H₂ present. In the meantime, the water content is significantly increased, suggesting that both reactions of 2CO + O₂ = 2CO₂ and 2H₂ + O₂ = 2H₂O are activated. Generally, the O₂ dissociation is believed to have a higher activation energy than the combination of CO or hydrogen with an activated O* atom on a catalytic surface. During the operando spectroscopy experiments, usually a small amount of CO₂ (10–20% as shown in Figure 3) can be observed upon the CO's introduction over the catalyst at low temperatures, which is due to the combination of CO with an activated O* atom on the catalytic surface. This process is a surface cleaning (reduction) process of catalysts by fuel (CO), similar to the hydrogen reduction, but to a lesser degree. If the temperature is held in this low range (<150 °C) for a stationary test, the decreasing of CO conversion over time would be expected since the active surface O* atom is depleted without a comparable rate of recovery. However, at higher temperatures, higher CO conversion is achieved upon the activated O₂ dissociation. More direct evidence of a higher activation energy for the O₂ dissociation was achieved in a similar study for a CO oxidation reaction under H₂ (2000 ppm CO, 7200 ppm H₂, and 10% O₂). An Arrhenius-type plot of CO₂ and water is shown in Figure 4 during a continuous temperature ramping process. A process with a higher activation energy is initiated at above 158 °C for both CO oxidation and H₂ oxidation reactions, which confirms the O₂ dissociation process with a higher activation energy.

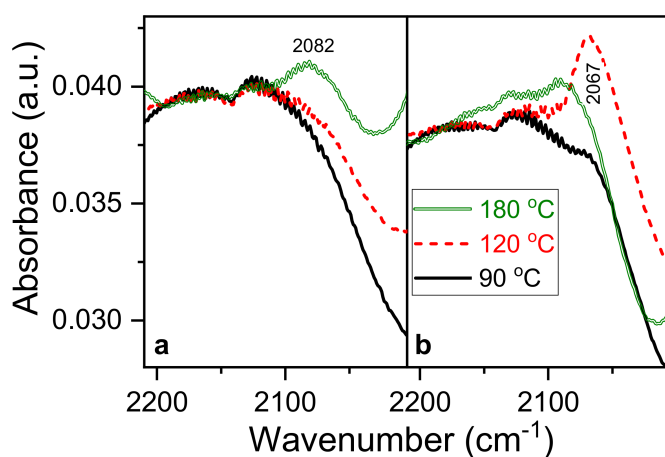


Figure 2. CO diffuse reflective infrared Fourier transform spectroscopy (DRIFTS) collected during CO oxidation reactions (CO 1000 ppm, O₂ 10%) (a) without and (b) with H₂ present (H₂ 2400 ppm) at 90, 120, and 180 °C.

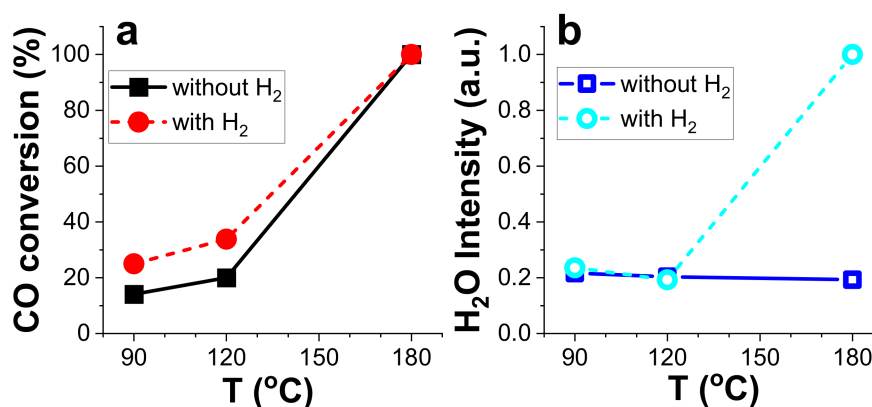


Figure 3. The activity results for (a) CO conversion and (b) water content collected during CO oxidation reactions (CO 1000 ppm, O₂ 10%) without (solid line) and with (dashed line) H₂ present (H₂ 2400 ppm) at 90, 120, and 180 °C.

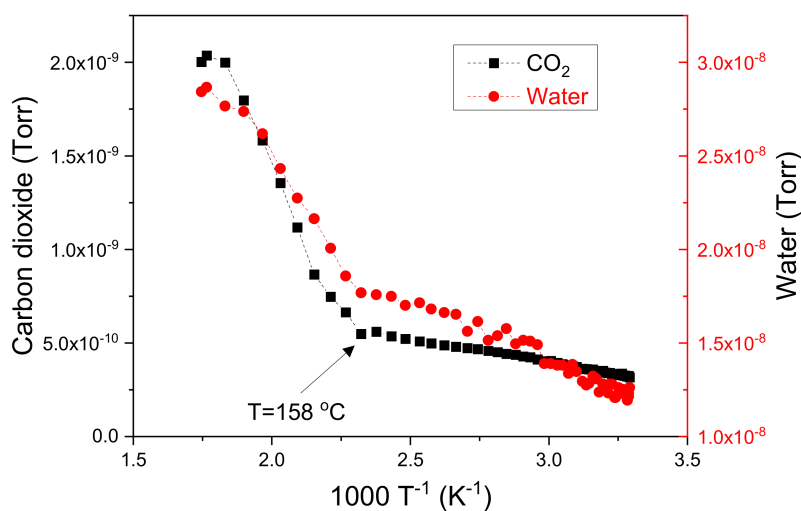


Figure 4. MS water and CO₂ signals as a function of $1/T$ for a DOC catalyst sample under a mixture of CO (2000 ppm), H₂ (7200 ppm), and O₂ (10%) balanced in Ar during cooling from 300 °C to 30 °C.

As a summary for the CO oxidation without the interference of NO_x , it can be concluded that the presence of hydrogen reduces the PGM surface, which in turn increases the CO conversion by 10–15% at low temperatures (90–120 °C). There is little competitive adsorption between CO and H_2 on the PGM surface, i.e., introduction of hydrogen does not remove adsorbed CO from PGM surfaces. Additionally, it was demonstrated that the O_2 dissociation has a higher activation energy than the combination of CO with active O^* , which can be activated at temperatures above 158 °C.

The second system that was explored was NO oxidation under the hydrogen impact at low temperatures. In general, NO under lean conditions passing through a DOC would be oxidized to NO_2 , which can be either released into the gas phase for the downstream selective catalytic reduction (SCR) or stored on the catalyst support as a nitrate species [15,26]. NO_x reduction is usually believed to be unfavorable because any reductant present would react first with the high concentration of O_2 in the diesel exhaust gas. This statement holds true at temperatures higher than the activation temperature for O_2 dissociation (i.e., 158 °C measured in our operando spectroscopy experiments as shown in Figure 4). In the following operando spectroscopy study, when the temperature is below the activated temperature for O_2 dissociation, the exception for NO reduction can exist under lean conditions. When a small amount of hydrogen is present, NO_x can undergo reduction reactions when the temperature is below 150 °C even in lean conditions with an excess of O_2 . Figure 5 shows the IR spectra in the range of 1200–1900 cm^{-1} with and without hydrogen for NO oxidation at 90–180 °C. A significantly larger amount of nitrate species (in the range of 1500–1700 cm^{-1}) are observed when H_2 is not present (Figure 5a vs. Figure 5c) since NO undergoes oxidation under this condition. The nitrate species are stable with similar IR peak intensities in the temperature range of 90–180 °C. However, when H_2 is present, gas phase N_2O as a NO_x reduction product is observed as shown in Figure 6 with higher intensities when T is below 150 °C. In the meantime, a small amount of nitrate species can be found from Figure 5c. These processes can be illustrated with the schematic drawings in Figure 5b,d for without and with H_2 impact, respectively. As a summary to NO oxidation under the hydrogen impact at low temperatures, the presence of hydrogen can inhibit the nitrate growth and promote NO_x reduction before O_2 dissociation is activated.

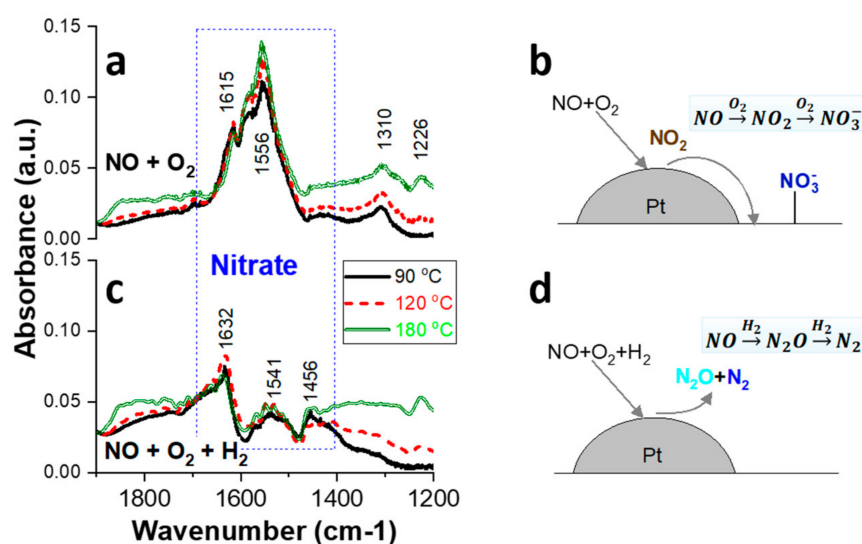


Figure 5. Nitrate spectra in Fourier-transformed infrared (FT-IR) collected during NO oxidation (NO 280 ppm, O_2 10%) reactions without (a) and with (c) H_2 present (H_2 2300 ppm) at 90, 120, and 180 °C, with their schematic mechanisms shown in (b,d), respectively.

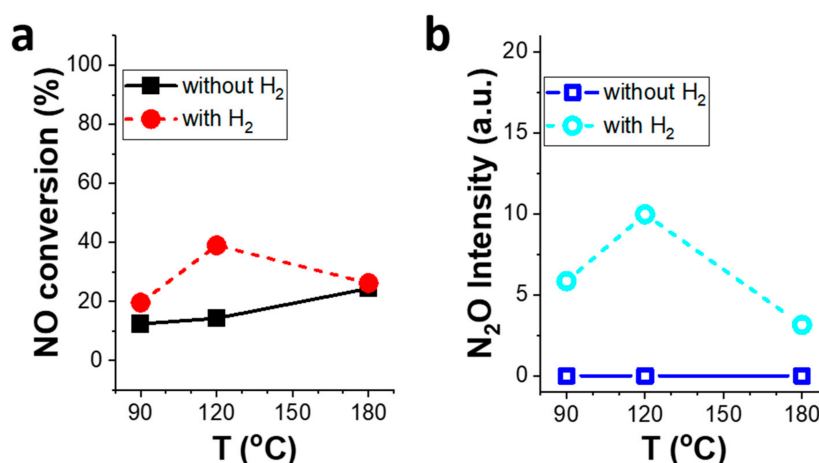


Figure 6. MKS and MS results for (a) NO conversion and (b) N₂O content collected during NO oxidation reactions (NO 280 ppm, O₂ 10%) without (solid line) and with (dashed line) H₂ present (H₂ 2300 ppm) at 90, 120, and 180 °C.

The third set of experiments was designed to investigate the hydrogen impact on CO oxidation under the interference of NO and/or NO_x at 90–180 °C [27]. In this section of the study, the following questions were addressed via operando spectroscopy: (1) NO/NO_x impact on CO conversion; (2) interaction between NO/NO_x and CO; and (3) hydrogen impact on CO oxidation with NO/NO_x present, which can be answered from the results shown in Figures 7–10 during the oxidation reactions of the CO and NO/NO_x mixture under hydrogen impact at 90–180 °C. Firstly, when H₂ is not present, the interaction between CO and NO is negligible with little N₂O (blue solid line in Figure 7c). Some N₂O is observed in the CO-O₂-NO_x experiment (blue solid line in Figure 7d) at 90–180 °C, which may come from the NO₂ self-decomposition and/or the CO and NO₂ interaction. The corresponding IR spectra in the nitrate region (Figure 8) suggest, in both cases (CO-O₂-NO and CO-O₂-NO_x), that a large amount of nitrate species grow on the catalyst, which indicates that the NO oxidation is dominating when H₂ is not present at 90–180 °C. With similar formation mechanisms as for Lean NO_x Trap materials, the nitrate, formed by NO oxidation at the PGM surface at 90–180 °C, is transferred to the support (illustrated in Figure 5b), which occupies the PGM-support interfacial sites (Figure 10). As a result, CO conversion (black solid lines in Figure 7a,b) is compromised at 180 °C after O₂ dissociation is activated.

However, when H₂ is present, almost no nitrate is built up in the case of CO-O₂-NO-H₂ reactions at 90–180 °C (Figure 8), and a much smaller amount of nitrate in the case of CO-O₂-NO_x-H₂ reactions at 180 °C (Figure 8). The decrease of nitrate build-up brings the CO conversion back to 100% and 70% at 180 °C for CO-O₂-NO-H₂ and CO-O₂-NO_x-H₂ reactions, respectively. In the meantime, more N₂O is observed at 180 °C in the MKS results shown as light blue dashed lines in Figure 7.

The relationship between the CO conversion and the nitrate growth at 180 °C was systematically investigated in Figure 9 with a total of eight experiments, as labeled in the x-axis. A reverse correlation between the CO conversion and the nitrate growth is clearly established. This result suggests that the interfacial sites between the PGM and the support materials are one of the major sites for O₂ dissociation and/or oxygen transfer. Once these sites are occupied by nitrate (stable at 90–180 °C), the CO conversion can be compromised by more than 50% (black solid lines in Figure 7 at 180 °C). The introduction of hydrogen inhibits the nitrate growth (Figure 10), which keeps the interfacial sites open for accessibility to active O* coming from O₂ dissociation and/or oxygen transferred from the support.

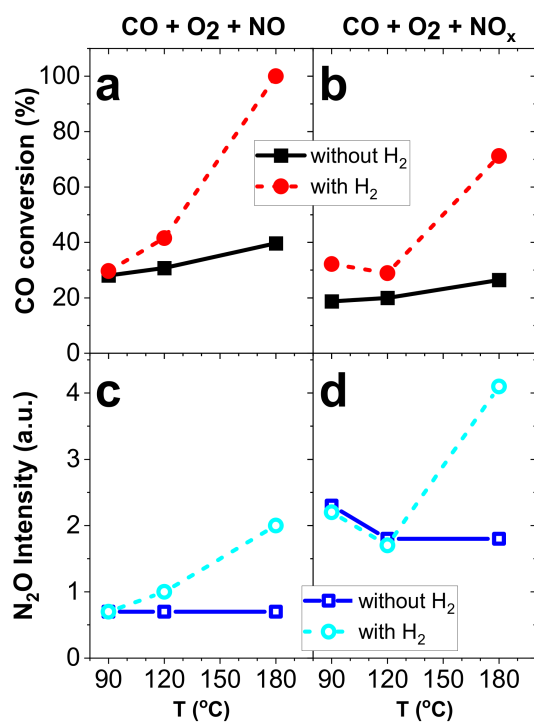


Figure 7. MKS results for (a,b) CO conversion and (c,d) N₂O content collected during CO oxidation reactions (CO 1000 ppm, O₂ 10%) under the impact of NO (a,c) (NO 280 ppm) and NO_x (b,d) (NO 280 ppm, NO₂ 190 ppm), without (solid line) and with (dashed line) H₂ present (H₂ 2300 ppm) at 90, 120, and 180 °C.

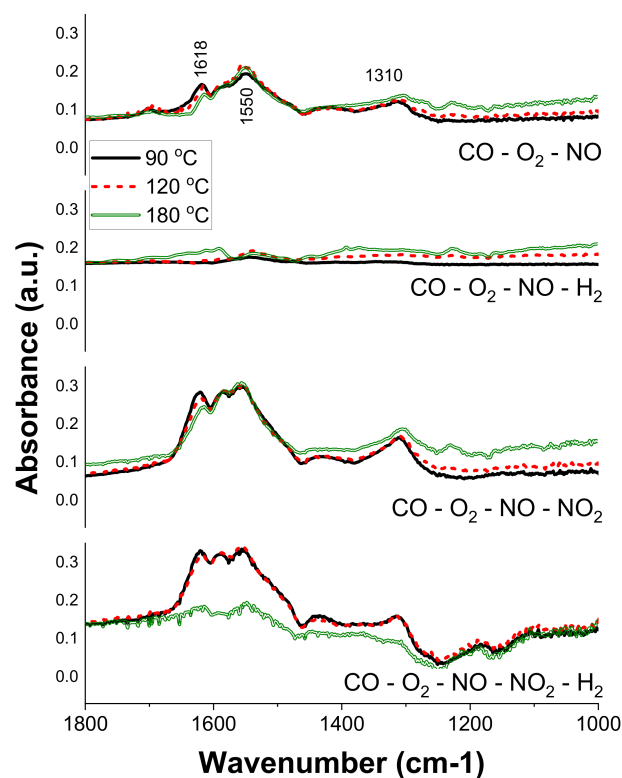


Figure 8. Nitrate spectra in the FT-IR collected during CO oxidation reactions under the impact of NO and NO_x, without and with H₂ present at 90, 120, and 180 °C.

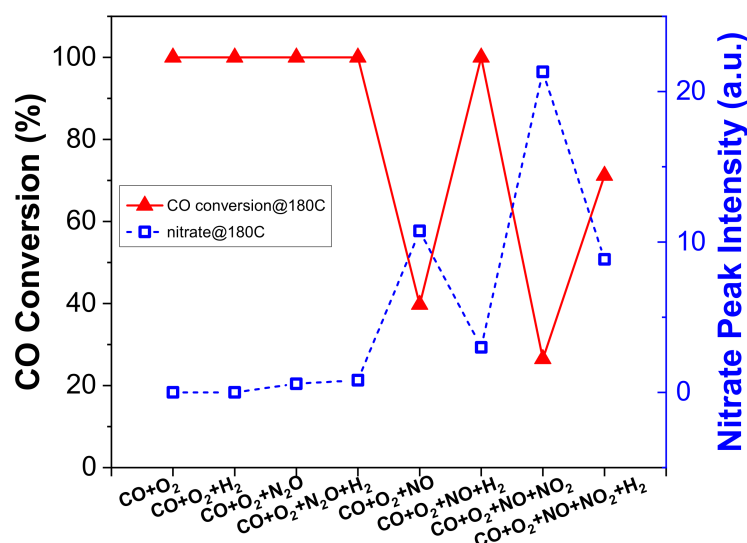


Figure 9. CO conversion and nitrate peak area in the FT-IR collected in different reactions at 180 °C, which indicates that the CO conversion is reversely impacted by the nitrate growth.

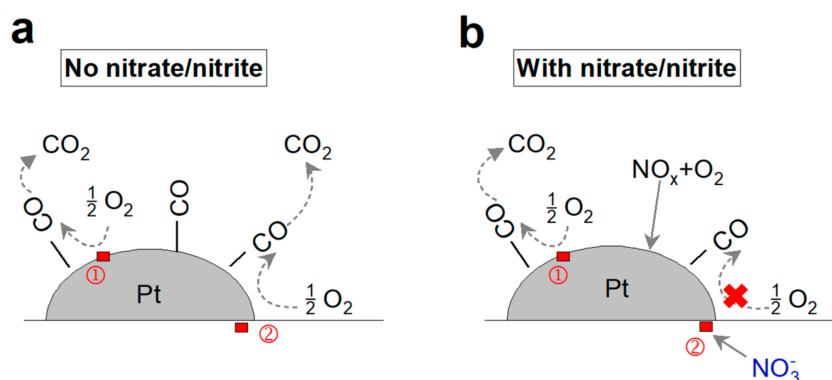


Figure 10. Schematic mechanisms show the CO oxidation without (a) and with (b) the impact of nitrate. When nitrate is populated at the platinum group metal (PGM)–support interface, the oxygen dissociation sites are occupied by nitrate, which causes the compromised CO conversion.

Through different combinations of reactions, a clear set of operando spectroscopic data and insights were obtained to fundamentally understand the hydrogen impact on the CO oxidation with the influence of NO_x over Pt/Alumina DOC catalysts. The results suggest that at the engine cold start temperature (90–180 °C), the nitrate growth can take away the PGM–support interfacial sites for O_2 dissociation and/or oxygen transfer, which compromises CO conversion. The introduction of hydrogen inhibits the nitrate growth, which keeps the interfacial sites open.

3. Materials and Methods

Sample information: The supported Pt/Alumina catalyst was prepared by an incipient wetness impregnation method using tetraamine platinum solution as a precursor and then calcined before a slurry preparation. The catalyst slurry was prepared by dispersing solid catalyst powders with binders in water phase with media milling to reach the desired particle sizes. The ball milling process was done by roller-type or small-media mills. Coated catalysts on honeycomb cores were prepared by the dip coating method, and then calcined at 550 °C for 3 h. The aged catalyst was treated at 800 °C for 16 h in 10% H_2O –10% O_2 balanced in N_2 . Aged ~1% Pt/alumina catalysts were scraped off from the coated cores.

Infrared Spectroscopy: DRIFTS experiments were performed on a *Varian 7000* FT-IR spectrometer (Santa Clara, CA, USA) equipped with an MCT detector and a Pike Technology high-temperature environmental chamber with a KBr window. Spectrum collection was performed under the diffuse reflection mode. The samples were ground into fine powders with a mortar and pestle, and then packed into the sample cup. The sample was dehydrated in Ar at 200 or 400 °C for 1 h with a ramp rate of 20 °C /min. IR spectra were collected after dehydration, once the chamber had been cooled to 30 °C.

Operando DRIFTS experiments were carried out on an *Agilent CARY680* FT-IR spectrometer equipped with a mercury cadmium telluride (MCT-HgCdTe) detector (Santa Clara, CA, USA) and a *Linkam* high-temperature environmental chamber with a calcium fluoride (CaF₂) window. The sample powder was dehydrated in flowing Ar or reduced in flowing 2.4% H₂/Ar at 400 °C for 1 h at a flow rate of 70 mL/min. The DRIFTS were collected during the operando reactions carried out at various temperatures. The absorbance spectra from the DRIFTS were ratioed to the background spectrum (the initial spectrum in Ar before reaction) and then used for analysis. In order to compare the DRIFTS data between the samples with different treatments (dehydrated vs. reduced), a common background spectrum in Argon on a KBr sample was used. The steady-state reactions for operando spectroscopy analysis were carried out under simplified gas feed compositions with a similar gas feed content of CO (1000–2000 ppm), O₂ (5–15%), NO_x (100–500 ppm), and/or H₂ (2000–3000 ppm) as for reactor testing conditions. The HC components are not considered in the operando reactions for simplicity. Additionally, due to the high sensitivity to moisture of the FT-IR spectrometer, the steam component was also removed in the operando reactions. A *Hidden Analytical* mass spectrometer (MS) (Livonia, MI, USA) and an FT-IR gas cell analyzer—*MKS MultiGas* (Andover, MA, USA) were used to monitor the gas phase components in the exhaust of the operando reactor.

4. Conclusions

A systematic operando DRIFTS Spectroscopy study was conducted to generate insights and develop a mechanistic understanding of the role of hydrogen on the CO oxidation over Pt/Alumina DOC catalysts as well as the influence of NO_x on this catalytic system that is of critical importance for the automotive industry. Based on the observed results, it can be concluded that the nitrate growth can occupy the PGM-support interfacial sites that are critical for O₂ dissociation and/or oxygen transfer at cold start temperatures for the engine (90–180 °C) and hinder CO conversion. The introduction of hydrogen on the catalyst surface inhibits the nitrate growth, which in turn keeps these critical interfacial sites open. The operando spectroscopic analysis and the identified mechanistic insights can guide the material and process developments for advancements in DOC catalyst design and application to meet the new regulations for low-temperature emission control.

5. Patents

A patent application was filed resulting from the work reported in this manuscript [27].

Author Contributions: Conceptualization, C.C.Z., B.Y.; Data curation, C.C.Z., S.H.; Investigation, C.C.Z. and S.S.; Methodology, C.C.Z. and B.Y.; Project administration, S.S., B.Y.; Resources, I.P., B.Y.; Writing—original draft, C.C.Z. and B.Y.; Writing—review & editing, S.S., I.P. and B.Y. All authors have read and agreed to the published version of the manuscript.

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