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Impact of Oxygen Storage Components in Prototype Pd-Based Three-Way Catalysts under Exhaust Conditions Relevant to Propane Engines [†]

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[†] This manuscript has been authored by UT-Battelle, LLC, under Contract No. DE-AC0500OR22725 with the U.S. Department of Energy. The United States Government and the publisher, by accepting the article for publication, acknowledge that the United States Government retains a non-exclusive, paid-up, irrevocable, world-wide license to publish or reproduce the published form of this manuscript, or allow others to do so, for the United States Government purposes. The Department of Energy will provide public access to these results of federally sponsored research in accordance with the DOE Public Access Plan (<http://energy.gov/downloads/doe-public-access-plan>).

Abstract: With increasing concerns about global warming, the push for sustainable and eco-friendly fuels is accelerating. Propane, recognized as liquefied petroleum gas or LPG, has garnered research interest as an alternative fuel due to its notable advantages, including a high-octane rating, reduced greenhouse gas emissions, and potential cost-effectiveness. However, to realize its full potential as an alternative fuel it is essential to develop catalysts that efficiently handle emissions at low temperatures. In our research, we investigated three distinct palladium (Pd)-based three-way catalyst (TWC) formulations (PdRh, Pd-only, and Pd-OSC) to investigate the influence of typical TWC components rhodium (Rh) and oxygen storage components (OSC) in exhaust scenarios relevant to propane-fueled engines. Among these, the formulation containing oxygen storage components (Pd-OSC) showed the highest reactivity for both NO and C₃H₈ while minimizing performance degradation from hydrothermal aging (HTA). Notably, the temperature of 50% conversion (T₅₀) for propane in the Pd-OSC fresh and HTA sample was lower by 30 °C and 13 °C, respectively, compared to the Pd-only sample, highlighting the role of oxygen storage materials in enhancing catalyst performance, even without dithering. Additionally, N₂ physisorption showed that the Pd-OSC sample has a higher surface area and increased pore volume. This underscores the idea that OSC materials not only augment the catalyst's porosity but also optimize reactant accessibility to active sites, thus elevating catalytic efficiency. In addition to evaluating performance, we further explored the performance and characteristics of the catalysts using catalytic probe reactions, such as water–gas shift and steam reforming reactions.

Keywords: propane engine; LPG; oxygen storage components; Pd-based three-way catalyst; water–gas shift reaction; steam reforming reaction



Citation: Kim, D.; Toops, T.J.; Nguyen, K.; Lance, M.J. Impact of Oxygen Storage Components in Prototype Pd-Based Three-Way Catalysts under Exhaust Conditions Relevant to Propane Engines. *Catalysts* **2023**, *13*, 1458. <https://doi.org/10.3390/catal13121458>

Academic Editors: Leonarda Liotta and Giuseppe Pantaleo

Received: 24 October 2023

Revised: 11 November 2023

Accepted: 20 November 2023

Published: 22 November 2023



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1. Introduction

In recent years, addressing climate change and reducing greenhouse gas emissions has become increasingly urgent. Governments around the world are implementing stricter emission regulations, driving the need for cleaner and more efficient combustion technologies. As a result, there has been growing interest in exploring alternative fuels that can meet or exceed these stringent standards, such as biodiesel, liquefied petroleum gas

(LPG), compressed natural gas (CNG), and liquefied natural gas (LNG) [1–5]. Among these alternatives, LPG has garnered attention as a viable alternative fuel source for internal combustion engines. Composed primarily of propane (C_3H_8), this hydrocarbon gas possesses properties that distinguish it as an environmentally friendly option. When compared to gasoline and diesel, propane combustion emits significantly fewer greenhouse gases (GHGs) and pollutants [6–8]. Although propane has a lower heating value per unit volume compared to gasoline, it reduces CO_2 emissions due to its decreased carbon content and minimizes nitrogen oxide (NO_x), carbon monoxide (CO), and particulate matter (PM) emissions through cleaner combustion [6,8,9]. Furthermore, propane's high-octane rating, low-carbon, and low oil-contamination characteristics have resulted in improved engine life, making it a preferred choice for high-mileage vehicles [10,11]. However, the high C–H bonding energy of C_3H_8 , along with methane (CH_4), imparts greater stability to propane compared to other hydrocarbon species, contributing to its reduced reactivity and oxidation activity within catalytic converters [12,13]. Therefore, to fully utilize propane as a viable alternative fuel, it is crucial to develop catalysts that can efficiently convert propane at low temperatures, especially during cold starts, while effectively managing NO_x and CO emissions.

The automotive industry has deployed three-way catalysts (TWCs) to meet emission regulations in stoichiometric gasoline-powered vehicles since the 1970s [14]. TWCs simultaneously catalyze the oxidation of CO plus hydrocarbons (HCs) while also reducing NO_x . Typically, TWCs are composed of noble metals like platinum (Pt), palladium (Pd), and/or rhodium (Rh), which are supported on a high-surface-area material like alumina and coated onto ceramic or metal monolithic structures. Pd, in particular, has been extensively utilized in TWCs due to its proficiency in reducing hydrocarbons and its enhanced resistance to thermal aging [14–16]. Additionally, TWCs contain oxygen storage components, often composed of cerium oxide (CeO_x) or other rare earth elements. These components are essential in maintaining the balance of oxidation and reduction reactions during the dithering process, thereby preserving optimal catalytic function amidst fluctuations in the air–fuel mixture. In addition, CeO_2 enhances the activity of water–gas shift (WGS) and steam reforming (SR) reactions, aiding in the removal of carbon monoxide and hydrocarbons [17]. However, the pure CeO_2 component in three-way catalysts (TWCs) faces challenges related to thermal stability and catalyst poisoning from impurities contained within the exhaust gases, as the harsh conditions of vehicle exhaust can lead to catalyst deactivation at high temperatures [18–20]. To overcome this limitation, the incorporation of ZrO_2 into the CeO_2 lattice has proven effective, preventing sintering and enhancing the oxygen storage capacity of the catalyst [21–23]. As a result, TWCs with ZrO_2 -incorporated CeO_2 exhibit better overall performance, maintaining catalytic activity and effectiveness across a wide range of operating conditions. Over the past few decades, three-way catalyst (TWC) technology has experienced significant advancements. While extensive research has been conducted on TWCs involving hydrocarbons such as methane and other gasoline-range hydrocarbons, there is a significant research gap regarding the specific evaluation of TWCs with a focus on propane (C_3H_8) as the sole unburned hydrocarbon (UHC). In particular, there remains a critical need to address the stability and reduced reactivity of propane within catalytic converters, especially during cold starts, because of the high C–H bonding energy of propane, along with methane. Therefore, dedicated research is necessary to comprehensively assess the catalytic conversion performance and optimize TWCs specifically for propane, aiming to maximize the utilization of propane as an alternative fuel for engines.

This study investigates the reactivity of three different formulations within a family of Pd-based prototype three-way catalysts (TWCs) to evaluate the effect of OSC and Rh on catalyst performance under exhaust conditions relevant to propane engines. Additionally, we investigate the impact of hydrothermal aging (HTA) on the performance of TWC samples under prescribed US-DRIVE aging conditions at 900 °C for 100 h. In addition to evaluating performance, the samples are analyzed using several catalytic probe reactions, including WGS reaction, SR reaction, and OSC assessments. The samples are further char-

acterized using scanning transmission electron microscopy (STEM) to determine particle size, as well as N₂ physisorption analysis to quantify surface area, pore volume, and pore size distribution. This research is expected to provide insights into the design of advanced catalyst systems for propane engines, paving the way for more sustainable and efficient utilization of propane as an alternative fuel.

2. Results and Discussion

2.1. Catalyst Structure

Table 1 presents the physical properties of three distinct formulations of a family of fresh and hydrothermally aged Pd-based TWC samples. It should be noted that the results include the weight of both the active catalyst layer and the non-porous monolithic substrate, which lowers the normalized values. Among the fresh samples, the Pd-OSC sample has a higher surface area and pore volume compared to the OSC-absent TWCs (PdRh and Pd samples), indicating that the presence of OSC materials could contribute to increased pore volume and, thus, increased surface area. This augmented porosity could potentially enhance the accessibility of reactants to active sites, thereby facilitating and bolstering catalytic reactions. Conversely, the pore size (determined by the Barrett–Joyner–Halenda or BJH method) for all TWC samples remains consistent, potentially due to uniform washcoat size across the samples. For hydrothermally aged samples, the Pd-OSC sample, even after aging, consistently maintains a higher pore volume compared to its OSC-absent counterparts, the PdRh and Pd samples. This sustained higher pore volume in the Pd-OSC sample, both before and after aging, underscores the enduring role of OSC materials in expanding the catalyst's pore structure. Importantly, this phenomenon maintains the access of reactants to active sites within the catalyst structure, potentially contributing to the preservation of catalytic activity. However, the reduction in BET surface area is more prominent in the Pd-OSC sample, closely resembling the BET surface area observed in the OSC-absent PdRh and Pd samples. This observation suggests that, while the presence of OSC materials may not entirely mitigate the reduction in surface area due to aging, it may still play a role in preserving other essential catalyst properties that are vital for sustaining overall catalytic performance.

Table 1. BET surface areas (S_{BET}), pore volumes, and average pore sizes of fresh and hydrothermally aged TWC samples.

Sample		S_{BET} (m ² /g)	Pore Volume * (cm ³ /g)	Average Pore Size * (nm)
PdRh	Fresh	28.5	0.11	12.6
	HTA	19.7	0.09	12.6
Pd-only	Fresh	28.4	0.12	12.6
	HTA	24.5	0.12	17.9
Pd-OSC	Fresh	43.9	0.22	12.6
	HTA	20.6	0.18	17.8

* Determined using Barrett–Joyner–Halenda (BJH) method.

2.2. Bench-Flow Reactor (BFR) Performance Assessment

To investigate the effect of including OSC materials, we conducted an analysis of oxygen storage in fresh and hydrothermally aged (HTA) samples for PdRh, Pd-only, and Pd-OSC catalysts. The oxygen storage experiment was conducted at temperatures of 350 °C and 550 °C; these results are depicted in Figure 1. As expected, for fresh samples, the oxygen storage of the Pd-OSC catalyst demonstrated a significant advantage over other catalysts at 550 °C. Notably, the Pd-OSC catalyst exhibited an OSC capacity approximately 6.8 times higher than that of the PdRh catalyst and roughly 2.4 times greater than that of the Pd-only catalyst. Even without OSC materials, oxygen storage was observed in the PdRh and Pd-only samples. This is primarily due to oxygen interacting with catalytic sites

on Pd and Rh, and thus the difference between the samples is not notable. Additionally, when examining the post-thermal aging results, notably higher oxygen storage for the Pd-OSC sample was observed at 550 °C. However, at 350 °C, Pd-OSC and PdRh exhibited similar oxygen storage, while the Pd-only sample had the highest capacity. This further highlights the importance of oxygen adsorption and desorption at Pd sites dominating at this lower temperature.

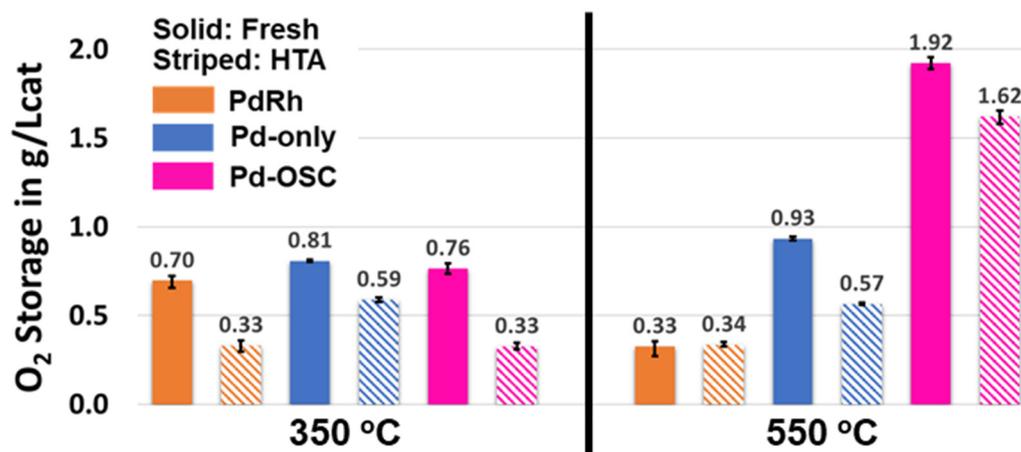


Figure 1. Oxygen storage capacity (OSC) for PdRh, Pd-only, and Pd-OSC TWC fresh (solid) and HTA (striped) samples.

Figure 2 displays the light-off curves for the conversion of NO, CO, and C₃H₈ for all TWC samples, along with the temperature of 50% conversion (T₅₀) for each gas species. Figure 2a,b reveal a marked augmentation in reactivity for the conversion of both NO and C₃H₈ when OSC materials are incorporated into the catalyst. This implies that OSC materials play a significant role in enhancing the catalytic oxidation and reduction processes for these gases. Furthermore, the catalytic performance of the Pd-OSC sample in terms of NO and C₃H₈ conversion remains superior, even after undergoing hydrothermal aging. Notably, when compared to the Pd-only TWC fresh sample, the Pd-OSC fresh sample exhibits lower T₅₀ values by approximately 32 °C and 30 °C for NO and C₃H₈ conversion, respectively. In other words, the inclusion of OSC materials within the catalyst composition helps maintain the structural integrity and catalytic activity of the Pd-OSC sample under the challenging conditions of hydrothermal aging. Therefore, these results underscore the potential of catalysts containing OSC materials, not only to improve the efficiency and lifespan of catalytic converters in automobile exhaust systems but also to reduce harmful emissions effectively, even under dithering conditions. This role in augmenting the catalytic oxidation and reduction processes for these gases makes them well-suited for propane engines. On the contrary, the TWC catalyst containing Rh (the PdRh sample) exhibited a significant decline in performance following the same hydrothermal aging process. This degradation in performance surpassed that observed in the other catalysts, indicating a potential formation of RhAlO_x species [24]. This formation is likely a major contributing factor to the reduction in catalytic activity post-aging, underscoring the sensitivity of Rh-containing catalysts to hydrothermal aging conditions; however, we were not able to attain any physical characterization to support this effect on these aged samples. Additionally, Rh is typically introduced to aid in the reduction in NO_x, but its benefit was not revealed here when propane was the sole HC. This suggests Rh's benefit will be lessened in propane emissions control, and that a TWC that is highly active with propane will be the most important attribute.

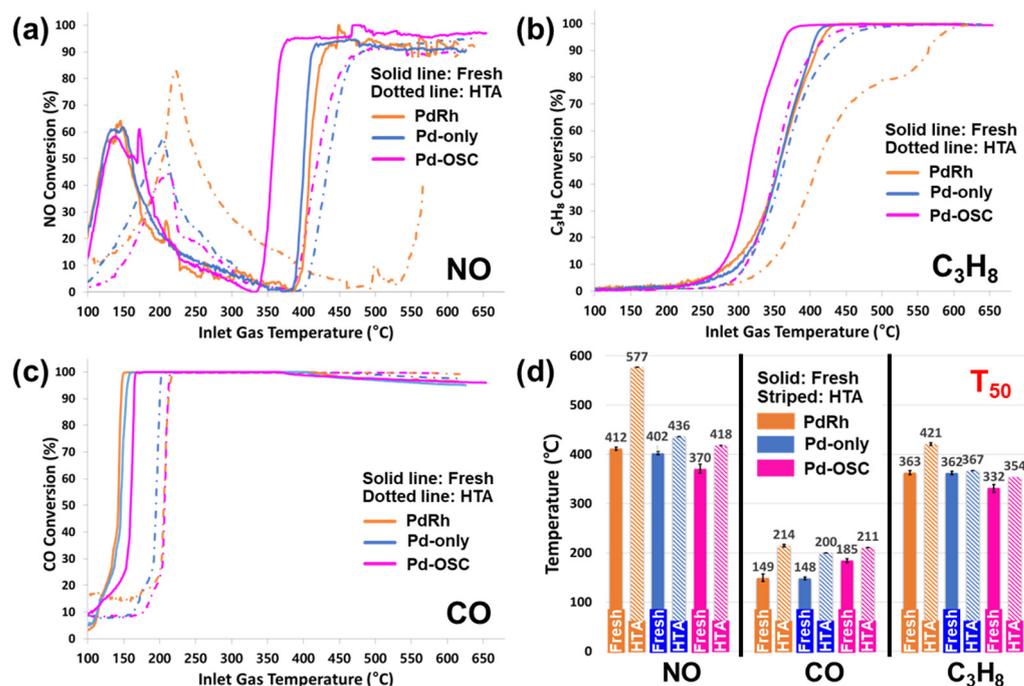


Figure 2. Effect of inlet gas temperature on the conversion of (a) NO, (b) C₃H₈, and (c) CO and (d) T₅₀ of each gas species for PdRh, Pd-only, and Pd-OSC fresh and HTA samples at stoichiometric condition.

Figure 3 shows the formation of NH₃ and N₂O for PdRh, Pd-only, and Pd-OSC samples. A particularly intriguing finding is the significantly earlier initiation of high-temperature NH₃ generation depicted in Figure 3a, at approximately 50 °C lower, in the Pd-OSC catalyst in comparison to its counterparts. This intriguing revelation hints at a possible interplay between the water–gas shift (WGS) reaction-generated hydrogen (H₂) and the NO conversion process, leading to the formation of NH₃. This pathway constitutes a pivotal factor contributing to the reduction in the initiation temperature of NH₃ synthesis. Consequently, the utilization of such catalyst formulations presents a promising approach to enhance the catalytic performance for reducing NO and C₃H₈ pollutants in exhaust emissions.

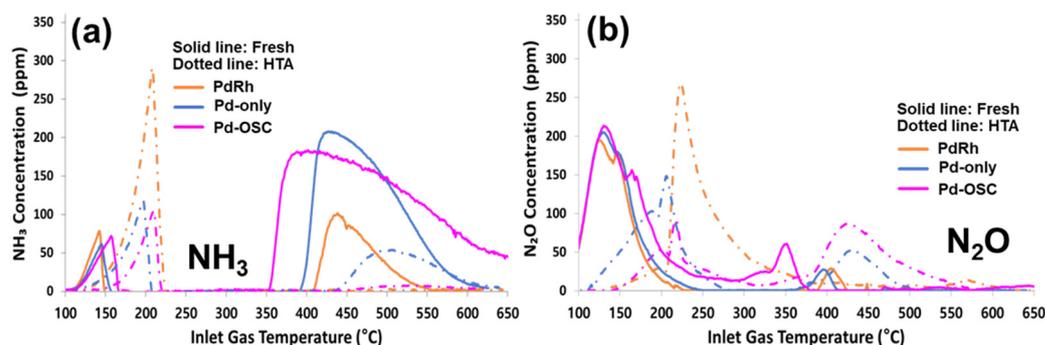


Figure 3. Effect of inlet gas temperature on the formation of (a) NH₃ and (b) N₂O PdRh, Pd-only, and Pd-OSC fresh and HTA samples at stoichiometric condition.

Figure 4 presents the water–gas shift (WGS) reaction for PdRh, Pd-only, and Pd-OSC samples between 200 and 600 °C at a rate of 5 °C/min. The Pd-OSC sample has higher activity from 200 to 400 °C, which can be attributed to the distinctive attributes of OSC materials, primarily their proficiency in adsorbing and releasing oxygen species throughout the catalytic cycle. OSC materials, as illustrated by the graph, serve as dynamic reservoirs of oxygen species, facilitating a more efficient exchange of oxygen during the

catalytic cycle. Consistent with several literature reports, the inclusion of OSC materials in Pd-based catalysts has been shown to enhance performance in the WGS reaction [17,25]. This heightened oxygen mobility results in a substantial increase in the conversion of CO and H₂O into CO₂ and H₂, thereby enhancing the overall performance of the water–gas shift (WGS) reaction. This suggests that H₂, produced during the redox cycle, actively participates in the NO reduction reaction, potentially contributing to the observed increase in NO conversion, as depicted in Figure 2a. However, Figure 5 illustrates a contrasting trend in the propane steam reforming (SR) reaction, where catalysts lacking OSC materials outperform Pd-OSC. In propane SR, the absence of OSC materials might lead to fewer competitive reactions, resulting in enhanced performance. Conversely, during the light-off process, characterized by the necessity for rapid initial conversion, Pd-OSC was more reactive due to its ability to facilitate oxygen transfer, thereby promoting rapid conversion. As observed in Figures 4 and 5, following hydrothermal aging, both WGS reactivity and SR reactivity degraded. Interestingly, for the fresh Pd-OSC samples, a notably enhanced WGS reactivity was observed compared to other samples. However, following HTA, this advantage diminished, with the Pd-OSC samples exhibiting comparable reactivity to other samples. For SR reactivity, the sample containing OSC materials (Pd-OSC) consistently showed lower reactivity than its counterparts. In both fresh and aged samples, the catalyst containing Rh (PdRh) displayed heightened SR reactivity, surpassing the performance of the other examined catalysts. This finding aligns with several studies [26,27] that have highlighted the enhanced SR reactivity inherent to Rh-utilizing catalysts. The consistently superior performance of PdRh accentuates the distinctive characteristics and benefits that Rh contributes to the SR process.

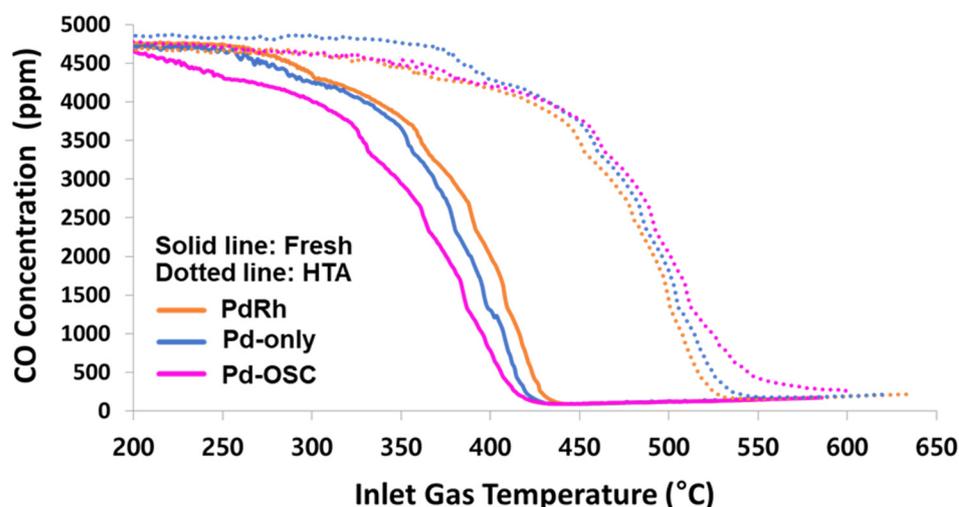


Figure 4. Conversion of CO in water–gas shift (WGS) reaction for PdRh, Pd-only, and Pd-OSC TWC fresh and HTA samples.

2.3. Scanning Transmission Electron Microscopy (STEM) Analysis

Figure 6 elucidates the dispersion and particle size of Pd within the catalyst samples using STEM imaging. In all fresh samples (Figure 6a–c), the Pd particles were highly dispersed and uniformly distributed throughout the sample. The size of these particles consistently measured under 5 nm. However, after undergoing hydrothermal aging (Figure 6d–f), there was a discernible alteration in their structure. Consistent with expectations, the Pd particles in these aged samples showed significant growth. The STEM visuals highlighted particle sizes surpassing 50 nm, signifying pronounced agglomeration or sintering during the aging process. Such an enlargement of particle size after aging further accentuates the pronounced impact of HTA on the structural evolutions of the catalyst.

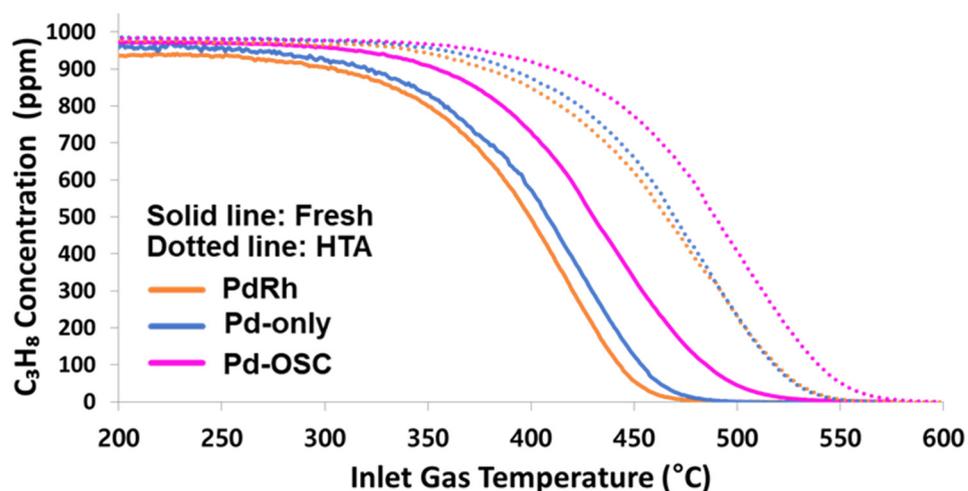


Figure 5. Conversion of C_3H_8 in steam reforming (SR) reaction for PdRh, Pd-only, and Pd-OSC TWC fresh and HTA samples.

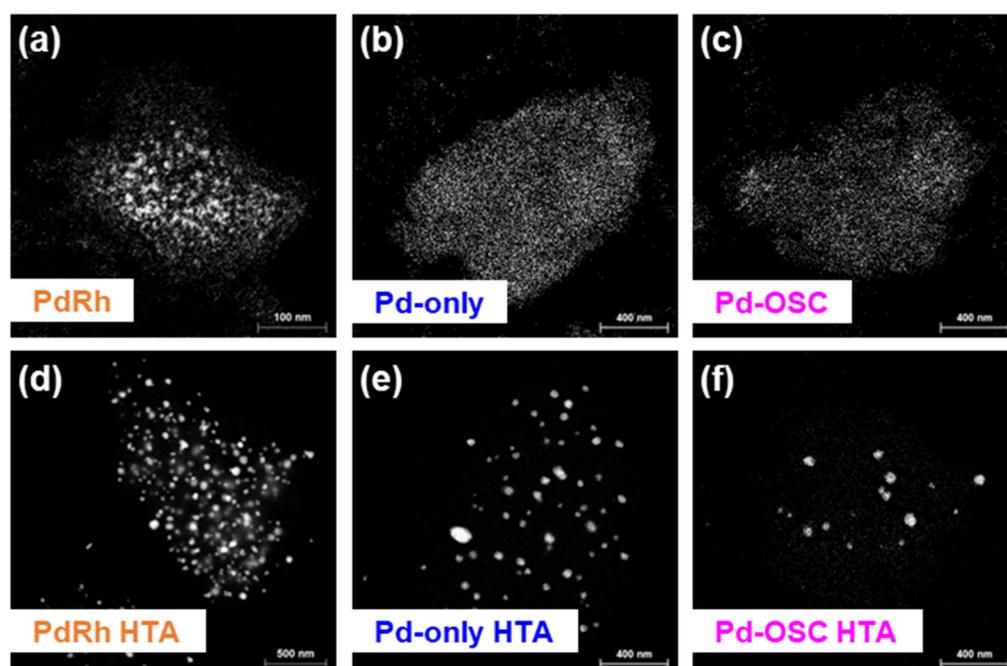


Figure 6. STEM images of Pd particles for PdRh, Pd-only, and Pd-OSC TWC fresh (a–c) and HTA (d–f) samples.

3. Materials and Methods

3.1. Three-Way Catalysts

Three distinct monolith formulations of three-way catalysts (TWCs) were employed in this study, each with a total PGM (platinum group metal) loading of 6.5 g/L. The samples are prototype formulations supplied specifically for this project by Umicore. The nomenclature of the samples and their respective catalyst compositions are presented in Table 2. The PdRh sample is characterized by a dual metal content of Pd and Rh with respective concentrations of 6.36 g/L and 0.14 g/L, and notably it is devoid of any OSC materials. The Pd-only version is singularly enriched with Pd at a concentration of 6.5 g/L and does not include OSC materials. The Pd-OSC sample is formulated with Pd at a concentration of 6.5 g/L and is complemented by the addition of OSC materials.

Table 2. Characteristics of PGM loading and OSC material in different samples.

Sample	PGM Loading (g/L)		OSC Material
	Pd	Rh	
PdRh	6.36	0.14	Absent
Pd-only	6.50	-	Absent
Pd-OSC	6.50	-	Present

3.2. Hydrothermal Aging

The catalyst samples were subjected to a hydrothermal aging procedure in a furnace set to 900 °C for a duration of 100 h, following the guidelines set forth by the Cross-Cut Lean Exhaust Emission Reduction Simulations (CLEERS) tailored for gasoline engines [28]. The process began in a neutral environment, consisting of 10% CO₂, 10% H₂O, and a balance made up of N₂, lasting 40 s. This phase was followed by a 10 s interval in rich conditions, characterized by 10% CO₂, 10% H₂O, 3% CO, 1% H₂, and a residual of N₂. The cycle concluded with another 10 s under lean conditions, incorporating 10% CO₂, 10% H₂O, 3% O₂, and a balance of N₂.

3.3. TWC Performance Evaluation Protocols

The detailed explanation of the experimental equipment for BFR has been discussed in a prior study [29]. BFR involves introducing individual gases that simulate exhaust emissions from a stoichiometric gasoline direct injection (S-GDI) engine into the system using mass flow controllers (MFCs). Deionized water is injected into a steam generator through a peristaltic water pump; this generator comprises a quartz tube enclosed in a Lindberg Minimate tubular furnace. A quartz tube TWC reactor with an outer diameter of 25.0 mm and a length of 46.0 cm was placed within the Lindberg Minimate furnace to control the simulated inlet gas temperature. To monitor temperatures, three omega type-K thermocouples were employed to measure the simulated exhaust gas temperature at the reactor's inlet and exit, as well as the middle of the catalyst (midbed) temperature. The concentrations of NO, CO, C₃H₈, CO₂, NH₃, and N₂O at the reactor's inlet and exit were determined using a MIDAC Fourier transform infrared spectroscopy (FTIR) analyzer.

Prior to the performance assessment on the BFR, the fresh TWC sample underwent a degreening procedure. This involved exposing the sample to an inlet temperature of 700 °C for a span of four hours, with a gaseous mixture consisting of 10% H₂O, 10% CO₂, with a balance of N₂. The light-off temperatures for NO, CO, and C₃H₈ were assessed under stoichiometric conditions using simulated exhaust gases. The gas composition included 1000 ppm C₃H₈, 0.5% CO, 0.1% NO, 0.167% H₂, 0.78% O₂, 13% H₂O, and 13% CO₂, with a balance of N₂. The temperature was ramped up from 100 °C to 600 °C at a rate of 5 °C/min. From the light-off curves, the 50% (T₅₀) and 90% (T₉₀) conversion temperatures were determined.

The performance of WGS and SR reactions, serving as probe reactions for the TWC, was assessed to understand the impact of the OSC material and the presence of Rh. Both reactions were evaluated under similar temperature conditions. A systematic temperature increase was employed, ranging from 200 °C to 600 °C at a consistent rate of 5 °C/min. For the WGS reaction, a gas blend of 0.5% CO and 13% H₂O, complemented by N₂, was utilized. Conversely, the SR reaction was examined using a mixture of 0.1% C₃H₈, 13% H₂O, with the balance being N₂.

To evaluate the oxygen storage capacity (OSC) of the catalysts, a method was employed that alternated between lean (comprising 1.5% O₂ and the remaining N₂ for a duration of 10 min) and rich phases (consisting of 0.2% CO and the residual N₂ for over 5 min). The assessment temperature started at 550 °C and was systematically reduced by 200 °C steps until reaching 150 °C. The OSC was calculated based on the amount of CO₂ generated

during rich phases. Detailed protocols for this calculation can be found in the research conducted by Kim [30].

3.4. Surface Characterization Studies

N₂ physisorption experiments were performed using a Quantachrome gas sorption system (Autosorb iQ) (Anton Paar, Tokyo, Japan) to characterize the pore structure and surface area of the catalyst samples. Prior to measurement, samples were outgassed at 300 °C for 4 h. The surface area was determined using the Brunauer–Emmett–Teller (BET) method, while pore volume and pore size distribution were evaluated using the Barrett–Joyner–Halenda (BJH) method.

Sample imaging and evaluation were performed with a FEI Talos F200X TEM/STEM set to an accelerating voltage of 200 kV. The instrument was used for in-depth microstructural insights and elemental assessments, emphasizing the evaluation of Pd dispersion and the determination of particle size, especially after hydrothermal aging.

4. Conclusions

The presence of oxygen storage capacity (OSC) in three-way catalysts (TWCs) significantly improves reactivity for propane engine-relevant emissions. Compared to other examined catalysts, the Pd-OSC sample demonstrated a distinct edge, indicating the pivotal role OSC materials play in enhancing the catalyst's reactivity with propane. Fresh Pd-OSC samples exhibited higher surface area and pore volumes, suggesting that OSC materials can enhance the catalyst's porosity. Such an improvement potentially aids the accessibility of reactants to active sites, amplifying catalytic reactions. During WGS reaction assessments, the Pd-OSC sample showcased remarkable performance, particularly in the efficient conversion of CO and H₂O into CO₂ and H₂, highlighting the role of OSC materials in facilitating oxygen exchange throughout the catalytic cycle. Conversely, in steam reforming (SR) reactions, TWCs without OSC materials exhibited better performance, indicating possible competition from OSC materials. However, Rh-inclusive TWCs (PdRh) displayed heightened reactivity in the SR process, emphasizing the unique contributions of Rh. Hydrothermal aging (HTA) is a critical consideration in the longevity and sustained performance of TWCs, especially when exposed to conditions simulating real-world engine operations. Over time, this aging process can lead to physical alterations, such as the sintering of active sites, which can compromise the structure and efficiency of the catalyst. As revealed by STEM imaging, after undergoing hydrothermal aging, all the TWC samples experienced significant sintering with particle sizes growing to over 50 nm. However, even after hydrothermal aging, the Pd-OSC TWC sample consistently exhibited superior NO and C₃H₈ conversion performance when compared to other samples that did not incorporate OSC materials. This persistence in performance further accentuates the advantages of integrating OSC materials into TWCs.

In conclusion, TWCs developed for application in propane engines should introduce significant OSC, and these results suggest that a thorough investigation of the optimal OSC loading could prove to be fruitful and perhaps even minimize the amount of Pd required in the TWC. OSC was beneficial in both initial reactivity and preserving functionality after HTA. In addition, it is anticipated that this oxygen storage and release mechanism would further enhance the Pd-OSC sample's performance in actual engine scenarios, such as during engine dithering, potentially offering better pollutant conversion rates than can be suggested by testing under stoichiometric conditions. Therefore, the utilization and further refinement of OSC-integrated catalysts can offer an efficiency benchmark in propane engine catalysis.

Author Contributions: Conceptualization, D.K., K.N. and T.J.T.; methodology, D.K., T.J.T. and M.J.L.; validation, K.N. and T.J.T.; formal analysis, D.K.; investigation, D.K.; resources, T.J.T.; data curation, D.K.; writing—original draft preparation, D.K.; writing—review and editing, T.J.T.; visualization, D.K. and M.J.L.; supervision, K.N. and T.J.T.; project administration, T.J.T. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the U.S. Department of Energy (DOE) Vehicle Technologies Office (VTO) via the Multi-Topic Funding Opportunity Announcement (FOA) No. DE-FOA-0001535. The authors gratefully acknowledge the support and direction of Kevin Stork, Siddiq Khan, Mike Weismiller, and Gurpreet Singh.

Data Availability Statement: Data are contained within the article.

Acknowledgments: FEI Talos F200X STEM provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program, and the Nuclear Science User Facilities.

Conflicts of Interest: The authors declare no conflict of interest.

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