FINAL TECHNICAL REPORT

NEXT GENERATION THREE-WAY CATALYSTS FOR FUTURE, HIGHLY EFFICIENT GASOLINE ENGINES

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EXECUTIVE SUMMARY

Ford Motor Company, Oak Ridge National Laboratory, and the University of Michigan completed a 3.25 year project on exhaust catalysts for gasoline vehicles that exhibit higher activity at lower temperatures down to 150°C. Ford has successfully used catalysts on cars and trucks to control emissions for over forty years. Changes in gasoline engine technology have allowed the use of "high tech" three-way catalysts (TWCs) to simultaneously control HC (hydrocarbons), CO (carbon monoxide), and NOx (nitrogen oxides) at nearly 100% efficiency. Excess fueling is used upon engine start to heat the catalyst up to its full operating temperature of greater than 350°C, lowering fuel economy and creating particulate matter. It was desirable to develop new catalysts for lower operating temperatures that may occur with future, more efficient gasoline powered vehicles, while still being durable to 150,000 mi with peak temperatures of 960°C. The work included laboratory preparation, aging, and poisoning of catalyst materials, activity tests, and chemical analyses. The objective of this project was to demonstrate progress toward the USDRIVE goal of achieving durable 90% conversion (T90) of hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NOx) at 150°C.

The project partners focused on several supported metal catalyst structures to promote lower light-off temperatures, enhance metal-support interaction, and improve durability. The raw materials (oxides of aluminum, cerium, silicon, titanium, and zirconium) were not new, but were used in novel ways. Palladium (Pd) or rhodium (Rh) were supported either on layered metal oxide supports, on nanoparticles, or used in various core@shell configurations. Catalyst materials were aged hydrothermally to a simulated high mileage. The catalyst formulation with the lowest durable light-off was 0.5 wt% Rh supported on alumina with an overlayer of either Ti or Zr. The temperatures for 90% conversion were up to 128°C lower than those of a commercial Pd three-way catalyst that had > 3x metal loading of the new Rh catalyst. An additional material made of Pd supported on nanoparticles of ceria-zirconia (CZO) was also considered; the aged T90s were up to 40°C lower than the commercial catalyst, at similar metal loading.

Further understanding of the catalyst architecture provided additional confidence to move forward with scale-up of 0.5 wt% Rh/Ti/Al_2O_3 to coated monolith laboratory cores for further evaluation. The team worked with Johnson Matthey to accomplish this, in addition to exploring manufacturability and potential costs. The overall benefit was estimated to be 10-15% lower NMOG and NOx tailpipe emissions on a cold start certification cycle.

INTRODUCTION

Ford Motor Company, Oak Ridge National Laboratory, and the University of Michigan completed a 3.25 year project on exhaust catalysts for gasoline vehicles that exhibit higher activity at lower temperatures down to 150°C. The project partners focused on several supported metal catalyst structures to promote lower light-off temperatures, enhance metal-support interaction, and improve durability. The raw materials (oxides of aluminum, cerium, silicon, titanium, and zirconium) were not new and were used in novel catalyst architectures. Palladium (Pd) or rhodium (Rh) were supported either on layered metal oxide supports, on nanoparticles, or used in various core@shell configurations. Catalyst materials were aged to a simulated high mileage at elevated temperatures with water present.

TECHNOLOGY BACKGROUND

Ford Motor Co. has successfully used catalysts on cars and trucks to control emissions for over forty years. Changes in gasoline engine technology have allowed the use of "high tech" three-way catalysts (TWCs) to simultaneously control HC (hydrocarbons), CO (carbon monoxide), and NOx (nitrogen oxides) at nearly 100% efficiency. Excess fueling is used upon engine start to bring the catalyst up to its full operating temperature of greater than 350°C, lowering fuel economy and creating particulate matter. It was desirable to develop new catalysts for lower operating temperatures that may occur with future, more efficient gasoline powered vehicles, while still being durable to 150,000 mi with peak temperatures of 960°C. The work included laboratory preparation, aging, and poisoning of catalyst materials, activity tests, and chemical analyses. The objective of this project was to demonstrate progress toward the USDRIVE goal of achieving durable 90% conversion (T90) of hydrocarbons (HC), carbon monoxide (CO), and oxides of nitrogen (NOx) at 150°C.

APPROACH

The approach used by Ford and its project partners (Oak Ridge National Laboratory, The University of Michigan, and Johnson Matthey, Inc.), was the following:

- Establish common test protocols between the project partners.
- Identify and characterize known, proven exhaust catalyst materials in new ways.
- Develop new catalyst formulations that improve PGM dispersion and promote activity after aging.
- Predict vehicle performance and finished catalyst cost.
- Leverage cross-laboratory analytical capabilities, including the Talos electron microscope at ORNL.

SCOPE

The project scope was originally proposed to cover three years and included subcontracts with Oak Ridge National Laboratory (ORNL) and the University of Michigan. A no-cost contract extension of three months was granted in 2017. The duration of the project then became October 1, 2014 through December 30, 2017, for a total of 3.25 years.

The main objective was to develop new catalysts for gasoline vehicle emission control operating at lower temperatures yet still durable to temperatures up to 960°C. The work included laboratory preparation, aging, and poisoning of catalyst materials, activity tests, and chemical analyses. The work resulted in new three-way catalysts (TWCs) and/or catalyst systems demonstrating significant progress towards durable 90% activity for hydrocarbon (HC), carbon monoxide (CO), and oxides of nitrogen (NOx) at 150°C.

The project consisted of three budget periods beginning October 2014 through December 2017. A description of each budget period is described below:

- ***Budget Period 1 (October 2014 – September 2015):*** The primary focus was to establish testing and aging protocols for catalyst materials and to benchmark a commercial TWC. The Recipient identified materials for establishing higher, durable catalytic surface area (e.g., modified metal oxide support materials, ternary mixed oxides, and Pd core@shell catalysts). Primary materials characterization was performed in multiple laboratories, and cross-lab characterizations were conducted. Computational models were updated for new material activity and used to predict TWC system performances. Finished catalyst costs and system costs were estimated.

- ***Budget Period 2 (October 2015 – September 2016):*** The work established in BP1 continued throughout BP2. Testing and aging protocols for catalyst materials were redefined as needed, and multiple benchmark TWCs were characterized. The Recipient worked with promising materials and/or any new materials identified in BP1 and combined promising materials from each partner where synergies were thought to exist. Computational models were updated, and finished catalyst and system costs were estimated.

- ***Budget Period 3 (October 2016 – September 2017 + 3 month extension to December 2017):*** This budget period began with a washcoat scale-up activity involving a major exhaust catalyst supplier, Johnson Matthey. A full aging and performance demonstration of core samples from coated monoliths was performed. Final performance model predictions and catalyst system costs were calculated.

ACCOMPLISHMENTS

Accomplishments are described under each of the key tasks outlined in the project summary above. Although project management efforts were present throughout, this report will focus on technical achievements. The technical areas included catalyst material development, modeling and laboratory scale prototype evaluations.

1 PROJECT MANAGEMENT

Project management activities were completed in accordance with the Federal Reporting Checklist as well as special requests such as Annual Merit Review and on-site meetings.

2 CATALYST DEVELOPMENT AND PERFORMANCE DEMONSTRATION

The intent behind the catalyst development tasks was to identify new material architectures that had the potential for lower light-off temperatures, termed T50 (temperature achieving 50% conversion) and T90 (temperature achieving 90% conversion). The team focused on materials that were already proven to survive exhaust gas temperatures, and used them in new ways. First, a commercial catalyst was aged at tested at Ford, then it was passed to each project partner to establish a correlation between reactors when using the same testing protocols. After this benchmarking exercise, new materials were tested based on modified oxide supports, base metal oxide combinations, and core@shell configurations. There was a downselection process to determine which formulations were ready for scale-up to washcoated monolith cores. Progress towards durable T90s of 150°C were quantified and compared to the benchmark.

2.1 Define Requirements and Testing Protocols

Recommended test protocols for catalysts operating under stoichiometric exhaust conditions were derived from the recommendations of the Advanced Combustion and Emission Control Tech Team of USDRIVE. Detailed test conditions were:

- 525 ppm ethylene (C_2H_4)
- 500 ppm propylene (C_3H_6)
- 150 ppm propane (C_3H_8)
- 1000 ppm nitrogen monoxide (NO)
- 0.5% carbon monoxide (CO)
- 0.17% hydrogen (H_2)
- 0.74% oxygen (O_2)
- 10-13% water (H_2O)
- 10-13% carbon dioxide (CO_2)
- Balance nitrogen (N_2)
- Ramp oven temperature up and down between 70°C and 500°C

2.2 Benchmark State of the Art TWC

The results of testing a commercial Pd-containing TWC sample at each partner are shown in Table 1. The catalyst was aged to a simulated high mileage condition on a so-called four mode aging schedule that is used by Ford Motor Company to rapidly simulate high mileage catalysts in a reactor that burns hydrocarbon-based fuels (pulse flame combustor). The air/fuel ratio was varied between stoichiometric, rich, and lean modes, with variation in temperature (Figure 1). Relatively good agreement was found for the T50 (temperature of 50% conversion) of each chemical species. It was confirmed that reactors at the three locations (including two at UM) were operating in a similar manner. In an example of the reactor output (Figure 2), the conversions of CO, various hydrocarbons, and NO may be noted, as well as formation of nitrous oxide (N_2O). It was also later confirmed that the reactors at Ford and JMI were well correlated using a different commercial sample.

Table 1. Cross-laboratory comparison of temperatures for 50% conversion (T50) for each chemical species over a commercial TWC.

	Species	UM 1	UM 2	ORNL	Ford
T50	CO	230	238	230	225
	C_2H_4	273	281	273	275
	C_3H_6	273	252	255	250
	C_3H_8	320	362	320	370
	NO	N/A	255	280	273

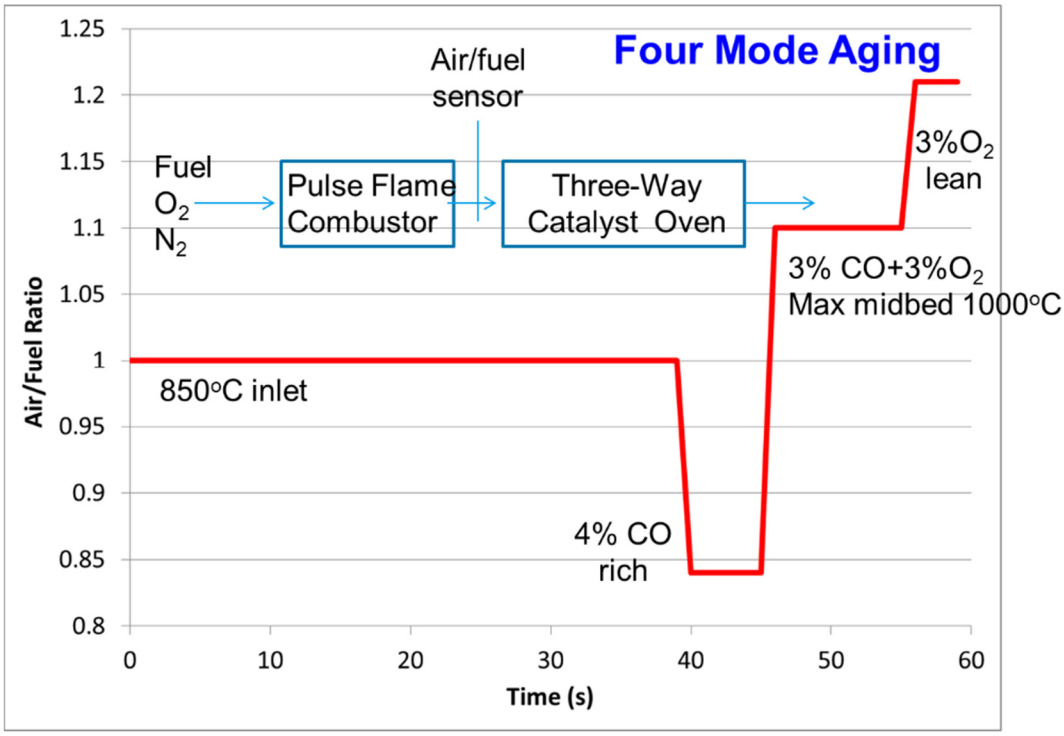

Figure 1. Four mode aging scheme used at Ford to rapidly create simulated high mileage catalyst materials. Fuel is burned to create exhaust gas in a reactor at stoichiometric and rich conditions, and CO and secondary O_2 are used to create lean air/fuel ratios.

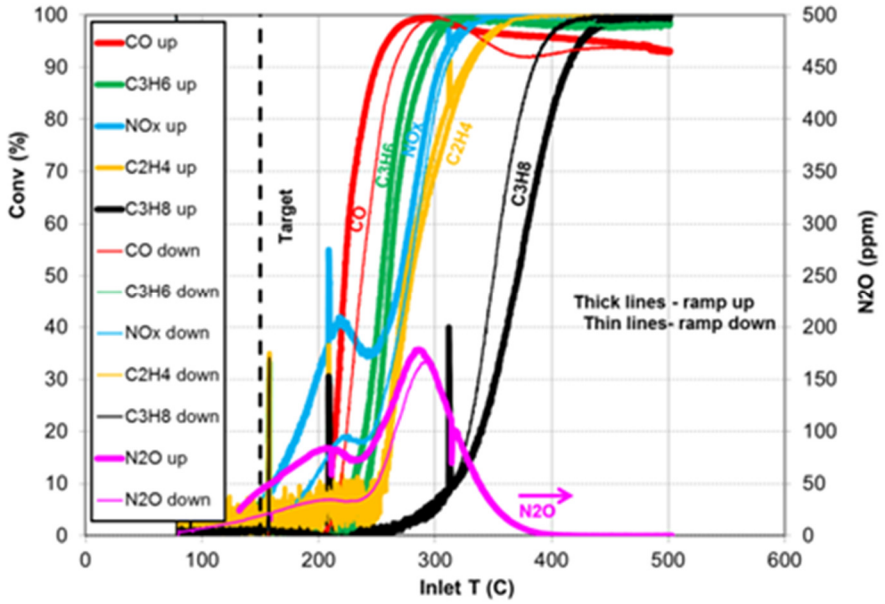

Figure 2. Aged TWC powder sample stoichiometric evaluation [1.8 g, 5°C/min ramp, C_3H_6, C_3H_8, C_2H_4, NO and CO, 3.5L/min]. The results are plotted against catalyst inlet temperature.

2.3 Synthesis and Characterization of Proposed Catalysts/Materials

The team focused on materials with durability to exhaust gas conditions, and used these materials in new ways. The emphasis was on maintaining higher surface areas and metal dispersions, while promoting beneficial precious-metal/support interactions. Oxide supports such as alumina (Al_2O_3), zirconia (ZrO_2), and titania (TiO_2) were modified for greater stability as mixed oxides or overlayers. Ceria-zirconia nanoparticles were used to support precious metals at high dispersion. Ternary base metal compounds were synthesized as potential precious metal replacements for low CO light-off. Finally, core@shell particles were made to prevent sintering of precious metal nanoparticles and serve as a potential barrier to inhibitors of low light-off temperature, such as HC poisoning of CO conversion. Samples were characterized for surface area and activity, and electron microscopy was used to confirm catalyst structure.

2.3.1 Modified Alumina/Zirconia/Titania Support Materials

One interesting way to create high surface area mixed oxide support materials is to begin with metal alkoxides and hydrolyze them in an aqueous solution, called sol-gel synthesis. Adding the active metal precursor before the oxides are formed is a one pot synthesis (Figure 3). Alternatively, the active metal may be added later via impregnation or incipient wetness techniques. Using these methods, Al_2O_3 with a stable surface area was obtained for an active and durable precious metal catalyst, and later a comparable support material was provided by a major material supplier.

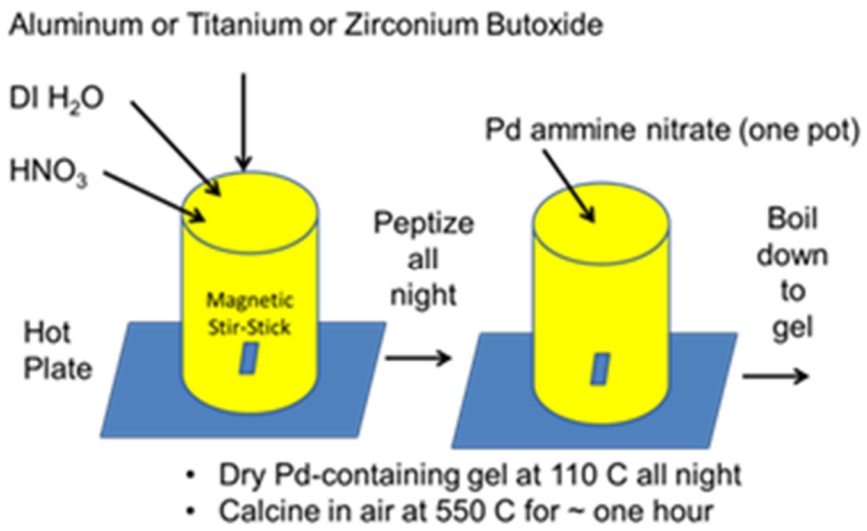

Figure 3. One pot synthesis of supported Pd catalyst material.

Next the team hypothesized that a layer of sol-gel derived titania or zirconia on Al_2O_3 may offer benefits for precious metal dispersion and metal-support interaction that could potentially lower light-off temperatures. This configuration is shown in Figure 4 compared to the conventional way of making supported metal catalysts with a bulk oxide. It was found that adding Pd resulted in T90s of 250-300°C (titania-containing example in Figure 5), with a notable large improvement in propane conversion over a commercial Pd TWC, while in the fresh state.

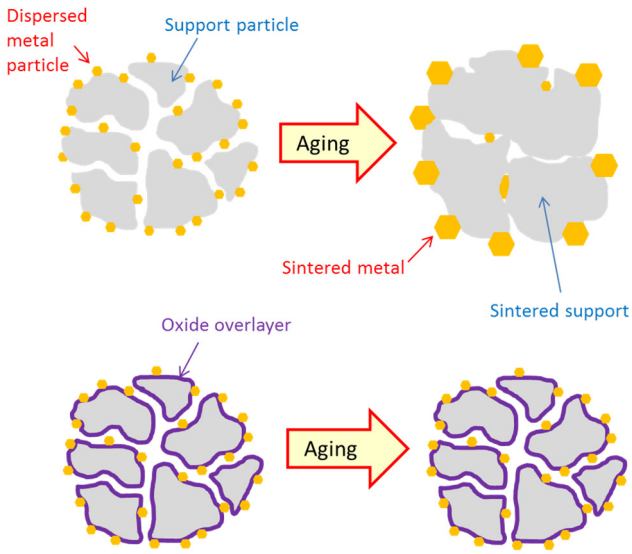

Figure 4. Approaches to creating supported metal catalysts using sol-gel synthesis with metal alkoxides. The top panel describes the conventional addition of precious metal particles to a bulk oxide, and the bottom panel illustrates the overlayer approach.

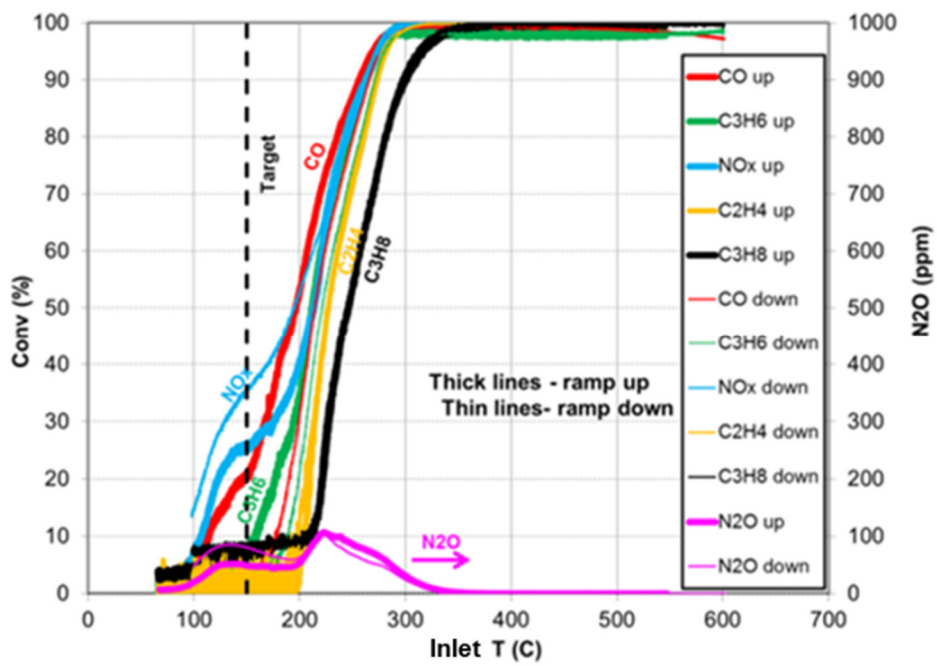

Figure 5. Reactor test with full exhaust mix for fresh 2 wt% Pd /8 wt% titanium (Ti)/ Al_2O_3. The results are plotted against inlet temperature. 1 g of sample was used with a gaseous flow rate of 3.6 L/min.

A zirconia overlayer version was also created and tested with similar benefits in the fresh state to the titania overlayer. A loading of 2 wt% Pd was chosen. Next, the Pd overlayer samples and a Pd non-overlayer sample were aged on the four mode aging schedule mentioned in Figure 1. The peak temperature during the aging was 960°C. After aging, the samples were tested for stoichiometric light-off behavior, and the overall behavior was similar between the Ford-prepared samples and the commercial sample (Figure 6). The data suggested that the overlayers did not prevent sintering of the Pd particles at 960°C. It was decided at that point to try Rh as the precious metal rather than Pd.

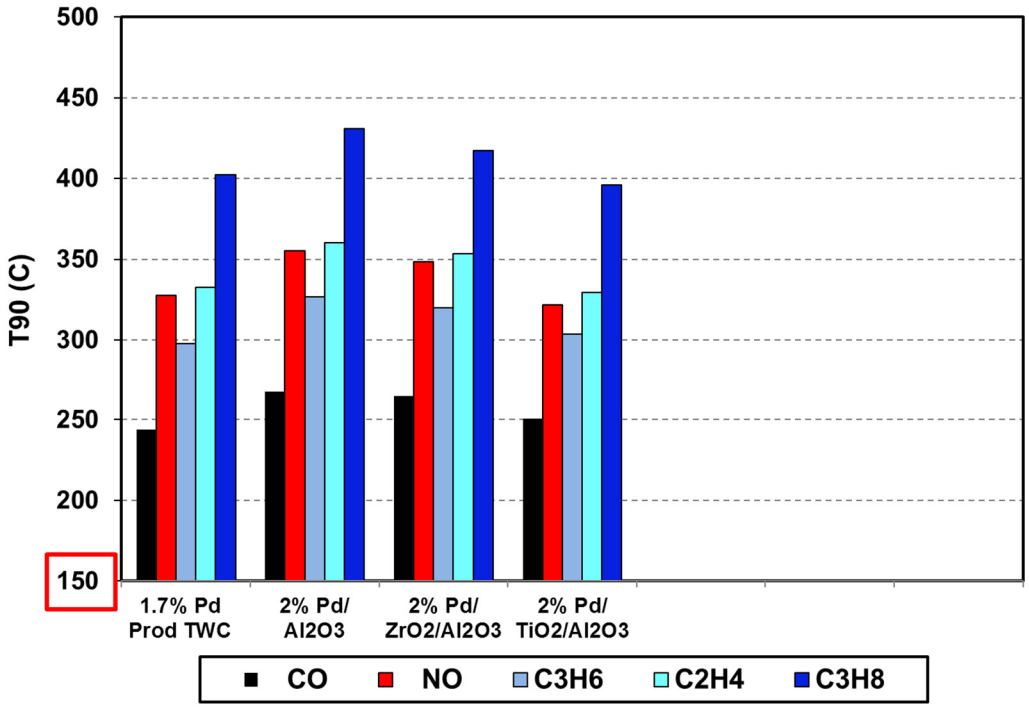

Figure 6. Light-off temperature results with a commercial Pd TWC (1.7% Pd Prod TWC) compared to Ford-prepared Pd/Al_2O_3 catalysts with and without overlayers.

Rh-containing catalysts were prepared in a similar manner to the Pd catalysts with and without overlayers of Zr and Ti. A lower loading (0.5 wt%) of Rh was chosen. Fresh light-off behavior looked promising so the samples were aged on the four mode schedule and retested (Figure 7). The Rh on alumina without any overlayer performed similarly to the Pd catalysts. However, when an overlayer of Zr or Ti was present, the light-off temperatures were 55 to over 100°C lower, with less than one third of the metal loading of the commercial sample (0.5 wt% Rh vs 1.7 wt% Pd).

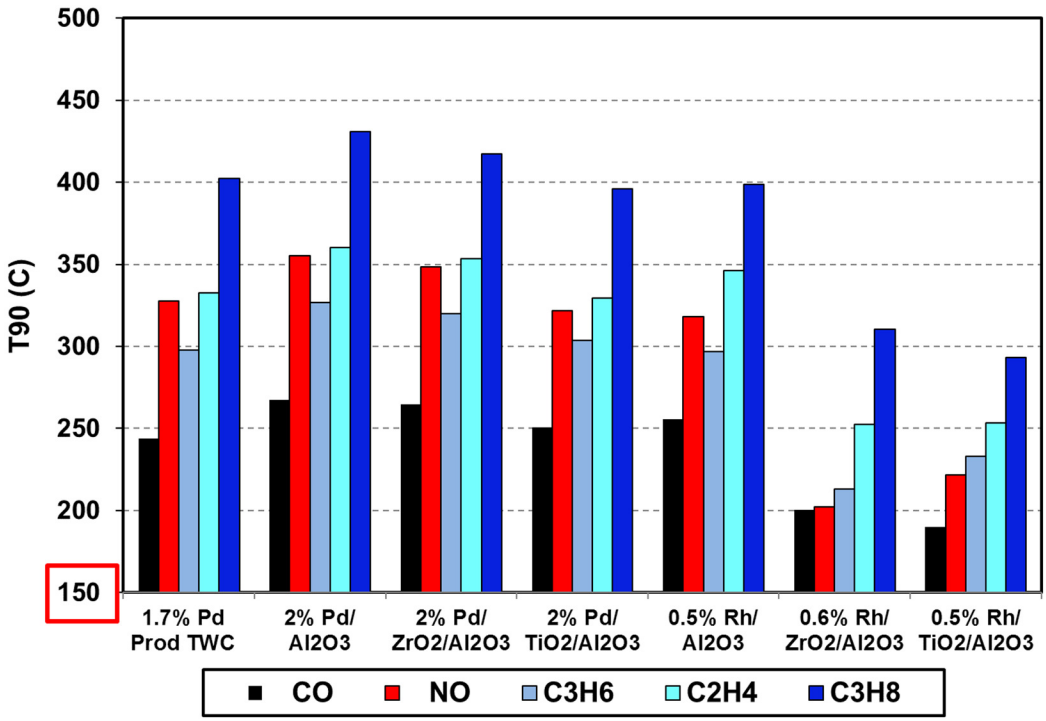

Figure 7. Light-off behavior for Rh-containing TWC samples prepared at Ford compared to Pd-containing samples. The commercial catalyst is included (1.7% Pd Prod TWC). All samples were aged to simulate high mileage on a four mode schedule in the lab reactor.

An optimization study was performed on the Rh and Ti contents. The sample made for the initial study was 0.5 wt% Rh and 8 wt% Ti; therefore, loadings both higher and lower than those values were selected. The T90 results with varied Ti content are shown in Figure 8. It was confirmed that 8 wt% was indeed the ideal Ti content for lowest light-off temperatures. Similarly, it was confirmed that 0.5 wt% Rh was ideal (Figure 9).

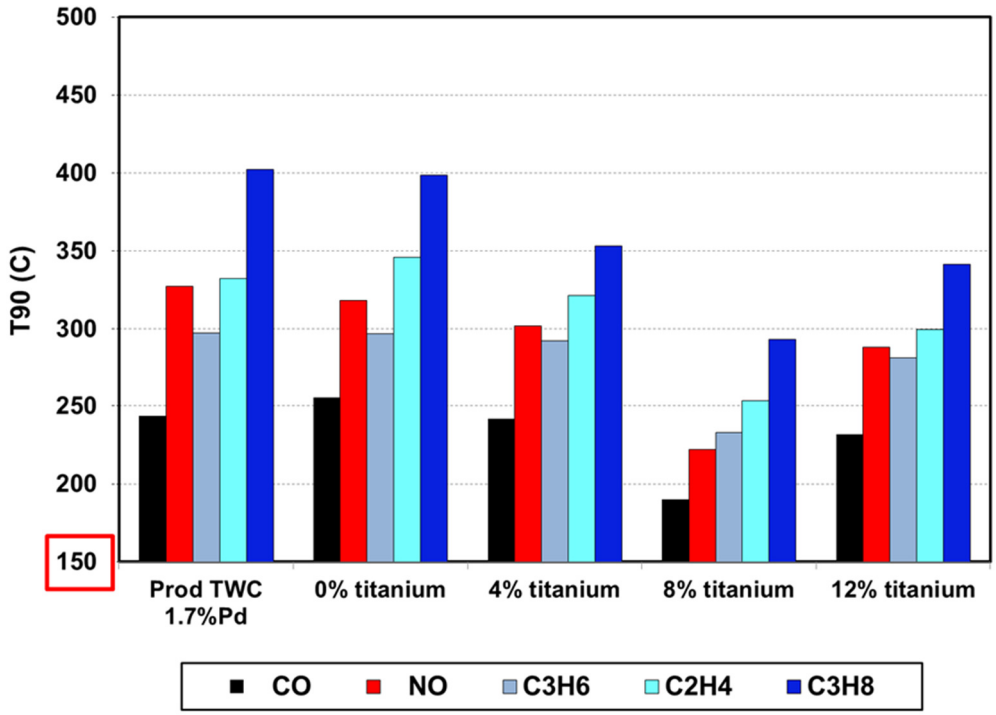

Figure 8. T90 results for four mode aged samples of 0.5 wt% Rh with varied Ti content as an overlayer on Si-stabilized Al_2O_3. The optimum Ti content was found to be 8 wt%.

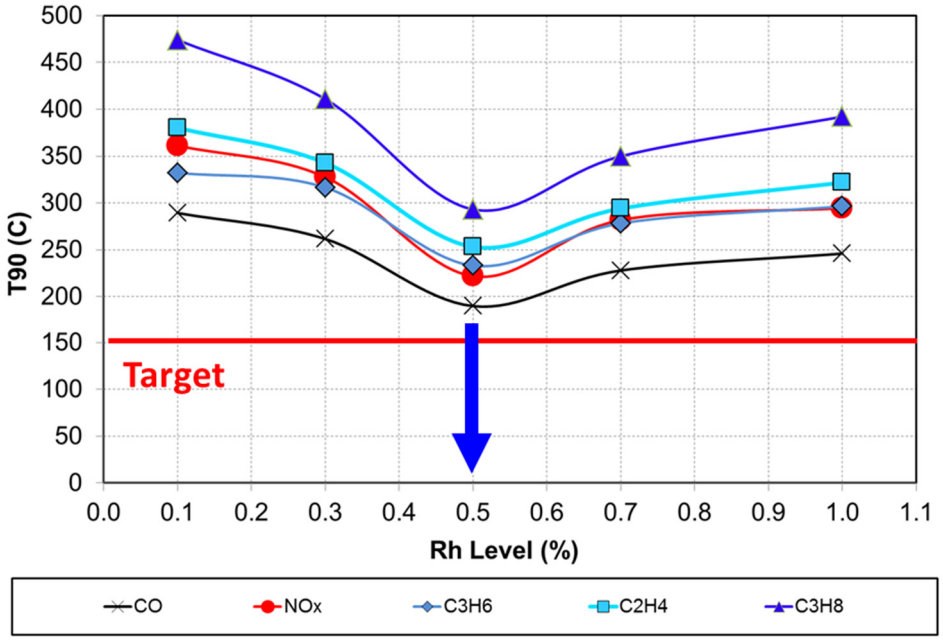

Figure 9. T90 results for four mode aged samples of Rh with 8 wt% Ti as an overlayer on Si-stabilized Al_2O_3. The optimum Rh content was found to be 0.5 wt%.

It was important to measure the impact of sulfur on the activity of the prime Rh TWC formulation, since sulfur is a known catalyst poison present in fuels and oils. Light-off tests were performed at stoichiometric conditions with sulfur (as SO_2), and no negative effect on T90s was found for most chemical species, including ethylene, as shown in the left panel of Figure 10. The only species that was negatively affected was propane. During a series of five tests, the T90s continuously degraded for propane (right panel of Figure 10). These data were taken when the sample was fresh. Subsequent data with a four mode aged sample showed a similar trend. Exposure to 600°C reversed or mitigated the effects of sulfur on the propane light-off. The Zr-containing version did not recover as easily as the Ti version and was kept as an alternate.

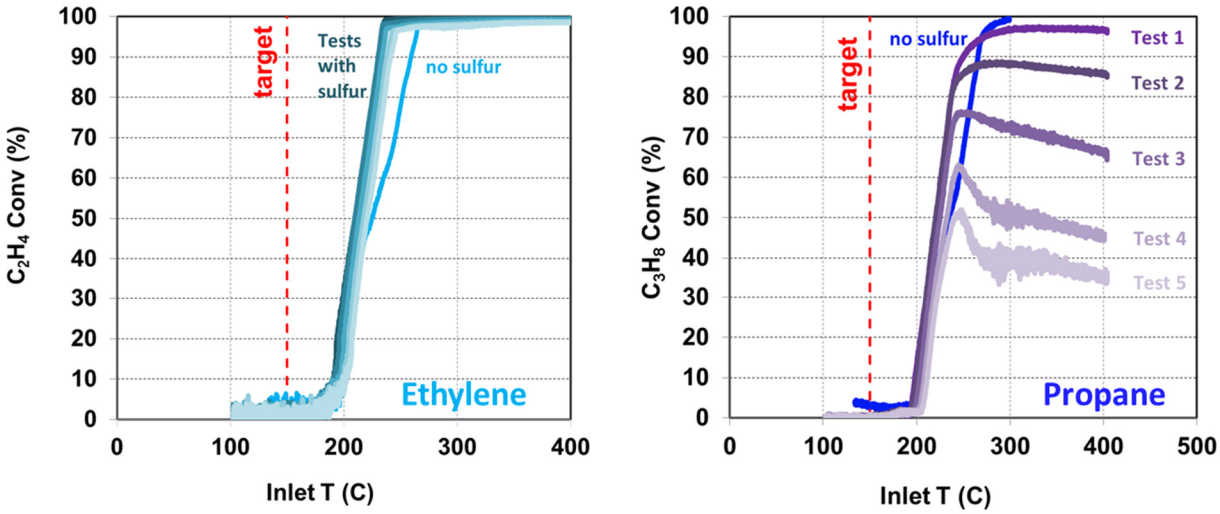

Figure 10. Impact of adding sulfur to stoichiometric reactor testing of 0.5 wt% Rh/8 wt% Ti/Al_2O_3. T90s for ethylene are included in the left panel, and T90s for propane are included in the right panel.

Electron microscopy was performed at Oak Ridge National Laboratory to confirm that the Ti was indeed an overlayer on the alumina particles and that Rh was well dispersed. Images of a fresh sample and two four mode aged samples are included in Figure 11. While this technique was by nature focused on very small areas of the catalyst surface, it was clear by looking at several locations and selecting representative areas to image that the Ti and Rh were well dispersed, even after high temperature exposure during aging.

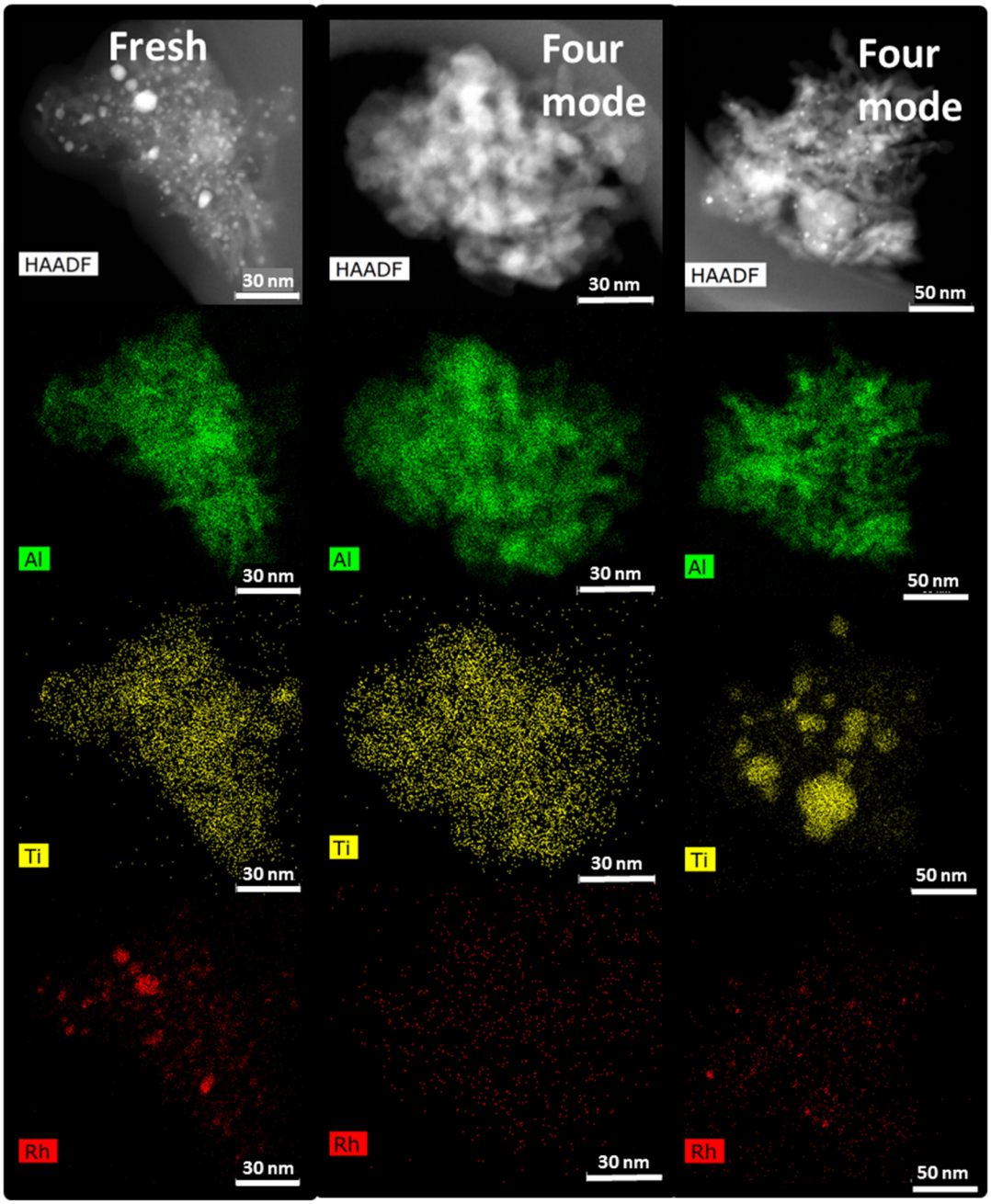

Figure 11. Electron microscopy of Rh/Ti/Si-alumina fresh and four mode aged (two different samples). Images obtained using the Talos F200X STEM at Oak Ridge National Laboratory, provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities).

To further understand the physical location of titania in the 0.5 wt% Rh/8 wt% Ti/Al_2O_3 material, the titania band gap energy was determined by diffuse reflectance UV-visible spectroscopy (DR-UV-vis). This technique can provide information about the degree of dispersion of the metal oxide, with isolated metal atoms having higher band gaps than particles composed of many atoms. Analysis of a sample containing 8 wt% Ti overlayer on alumina revealed a higher band gap than that of bulk titania, suggesting the Ti overlayer consisted of metal oxide clusters of < 100 atoms, and possibly fewer than 10 atoms (Figure 12).

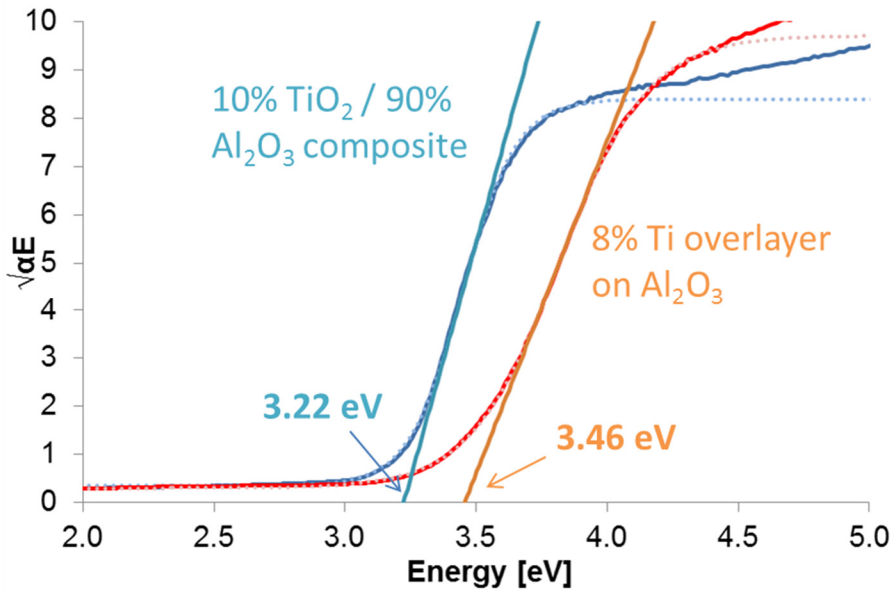

Figure 12. Diffuse reflectance UV-visible spectroscopy on 8% Ti overlayer on stabilized alumina (red) and on a sample containing 10 wt% of colloidal anatase physically mixed with alumina (blue) Straight lines are extrapolated band gap energies. Dotted lines are fits to the adsorption edge.

As explained in Figure 12, the band gap of the sample containing 10 wt% colloidal anatase in alumina was 3.22 eV, consistent with the known 3.2 eV band gap of bulk anatase. The band gap of the 8 wt% titania overlayer support was higher, at 3.46 eV. Since DR-UV-vis averages over all absorbers in the sample and alumina does not absorb UV light below 5.5 eV, it could be concluded the large majority of the titania in the overlayer was present in particles smaller than 2 nm. This was consistent with the observed high dispersion in the TEM image (Figure 11), as well as previous failures to observe these particles by X-ray diffraction. XRD is generally limited to particles > 5 nm.

It was known that a fully formulated three-way catalyst would need to have oxygen storage components to better handle oscillations in air/fuel ratio onboard a vehicle during transient operation. Nanoparticles of ceria-zirconia (CZO) were chosen that would serve this function as well as provide a high surface area to support precious metals. Ideally the resulting material would also contribute significant TWC activity at lower temperatures. A novel catalyst configuration was synthesized in which CZO nanoparticles were supported on a stabilized alumina, with Pd particles placed on the CZO. A schematic of the process is shown in Figure 13. The catalyst configuration was confirmed via electron microscopy (Figure 14).

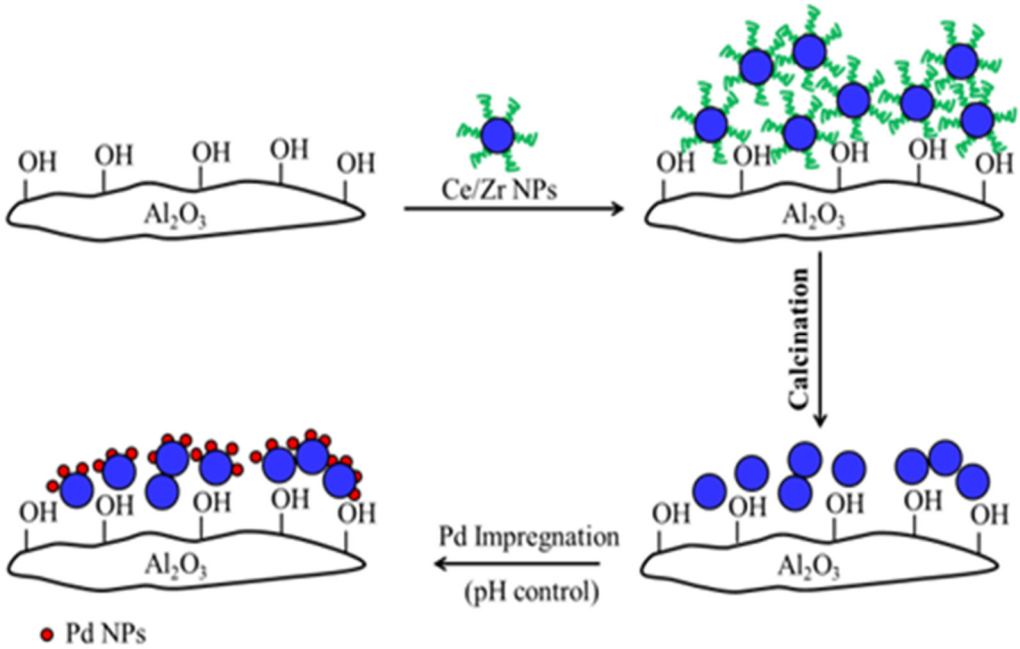

Figure 13. Synthesis process of adding ceria-zirconia (CZO) nanoparticles to a stabilized alumina support, and then impregnating Pd onto the CZO.

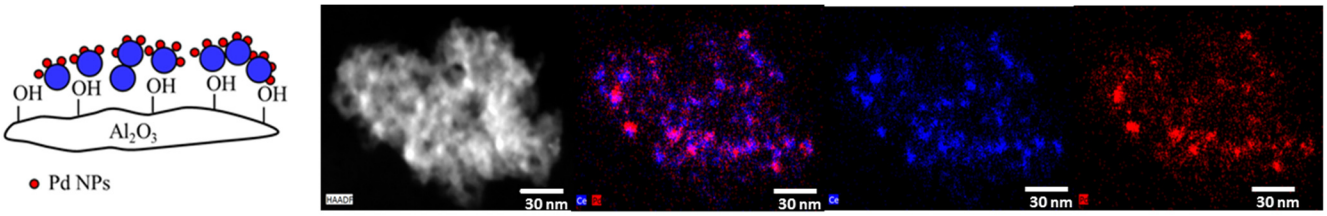

Figure 14. Electron microscopic images of Pd supported on well dispersed CZO nanoparticles on an alumina support. Images obtained using the Talos F200X STEM at Oak Ridge National Laboratory, provided by the Department of Energy, Office of Nuclear Energy, Fuel Cycle R&D Program and the Nuclear Science User Facilities).

A series of catalysts was prepared by loading an Al_2O_3 support with nano-CZO followed by deposition of various precious metals. The following precious metal types and loadings were synthesized and tested: 1 wt% Pt, 2 wt% Pt, 2 wt% Pd, 4 wt% Pd, and 0.5 wt% Rh. Figures 15 and 16 show the T50s and T90s of these catalysts after degreening and testing under USDRIVE protocols. The highest light-off temperatures were found with the 0.5 wt% Rh sample. Overall, the Pd and Pt-containing samples had the best activity, and it was decided to go forward with 2 wt% Pd and 1 wt% Pt for aging and further testing.

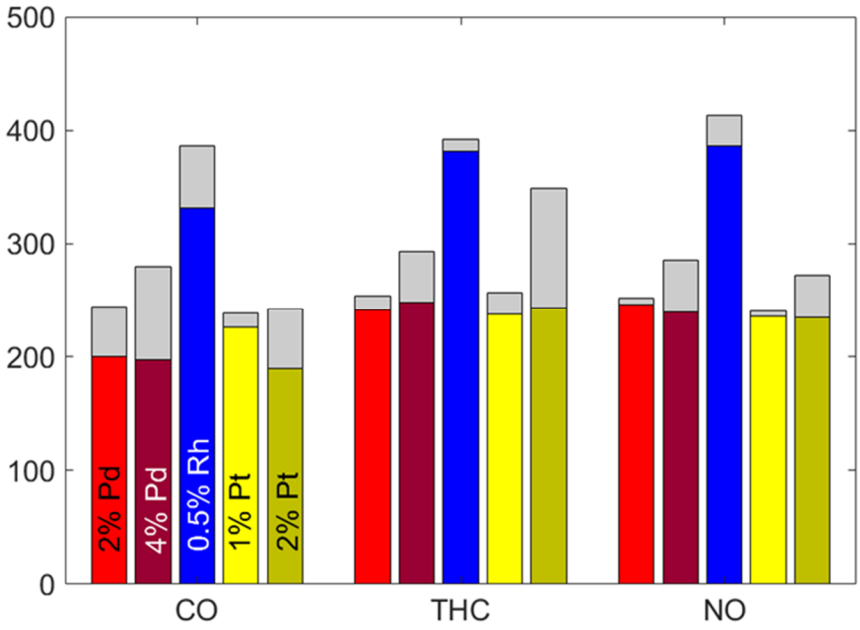

Figure 15. T50s and T90s for CO, total hydrocarbon (THC), and NO conversion over nano-CZO/Al_2O_3 with various PGM types and loadings.

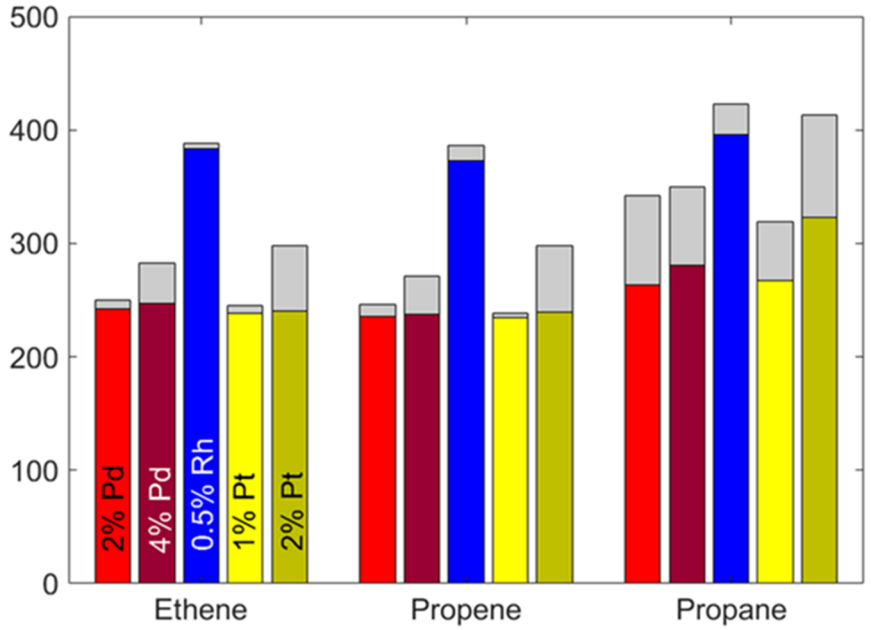

Figure 16. T50s and T90s for hydrocarbon species conversion over nano-CZO Al_2O_3 with various PGM types and loadings.

The aged light-off behavior for CO, NO, and total hydrocarbon (THC) is included in Figure 17. The sample of 2 wt% Pd/nano-CZO/Al_2O_3 was aged at 900°C in the presence of water and low oxygen conditions.

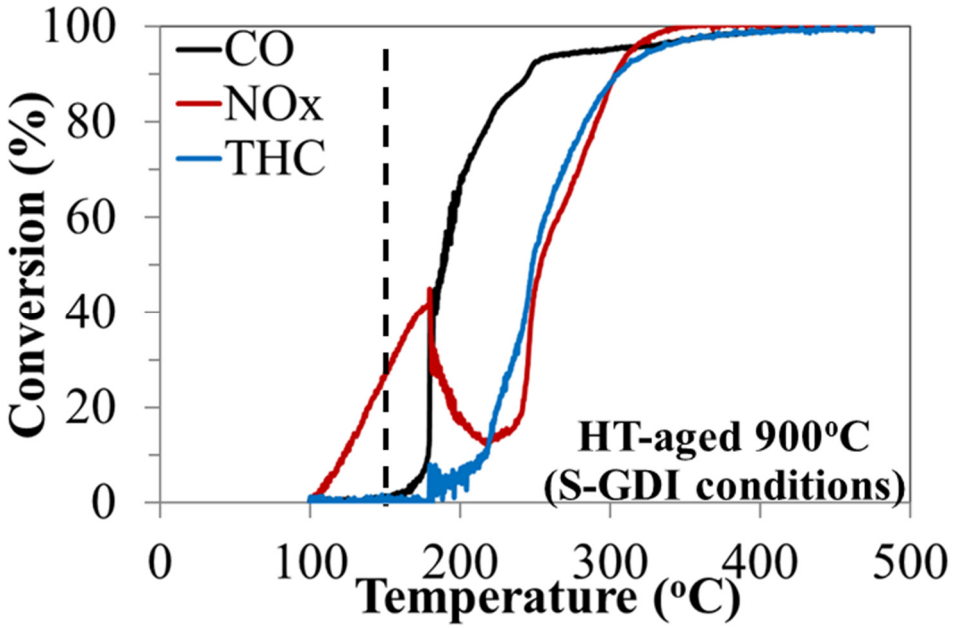

Figure 17. Aged light-off behavior for 2 wt% Pd/nano-CZO/Al_2O_3. The sample was aged at 900°C under stoichiometric (low O_2) hydrothermal conditions.

A summary of the T90s for the most promising materials from the stabilized metal oxide studies are included in Table 2. These materials were selected for scale-up to monolith cores.

Table 2. Temperatures for 90% conversion of carbon monoxide, hydrocarbons, and nitrogen oxide. A commercial TWC performance is compared to program materials. All samples were aged to simulate high mileage on a gasoline vehicle.

	1.7% Pd comm. TWC (960°C 4-mode)	**0.5% Rh/Ti/Al_2O_3 (960°C 4-mode)**	**0.6% Rh/Zr/Al_2O_3 (960°C 4-mode aged)**	**2% Pd/nano-CZO/Al_2O_3 (900°C stoich. aged)**	**1% Pt/nano-CZO/Al_2O_3 (900°C stoich. aged)**
T90 CO	245°C	190°C (-55°C)	201°C (-44°C)	245°C (0°C)	252°C (+7°C)
T90 HC	345°C	253°C (-92°C)	256°C (-89°C)	305°C (-40°C)	280°C (-65°C)
T90 NO	330°C	222°C (-108°C)	202°C (-128°C)	298°C (-32°C)	277°C (-53°C)

2.3.2 Modified Silica Support Materials

Another example of mixed oxide synthesis is presented in Figure 18 in which a shell of a low surface area material (ZrO_2) was formed on a core of high surface area material (SiO_2). Scanning transmission electron microscopy (STEM) confirmed the core-shell structure was obtained (Figure 19). A $Pd(NO_3)_2$ precursor was impregnated (incipient wetness) onto the SiO_2@ZrO_2 oxide support, leading to 1 wt% Pd/SiO_2@ZrO_2 catalysts. The fresh T50 for CO under lean conditions was around 200°C. Sulfur exposure negatively affected the T50, and the fresh activity was recovered after lean desulfations at 600, 700 and 800°C. The sample was also stable under longer term (16 h) hydrothermal aging at 800°C (Figure 20).

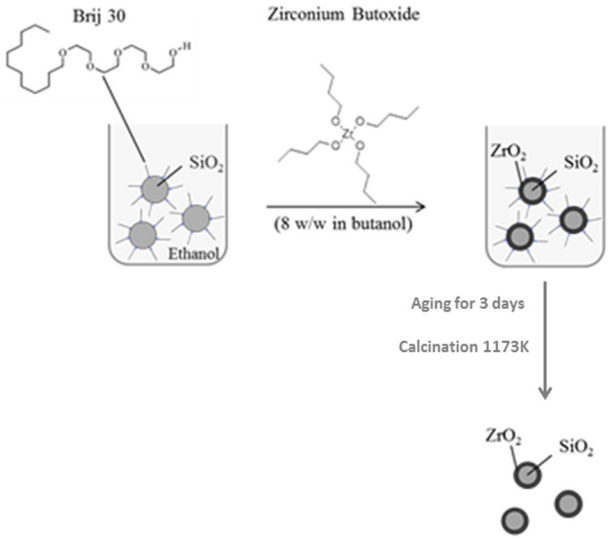

Figure 18. Synthetic procedure of SiO_2@ZrO_2 oxide supports.

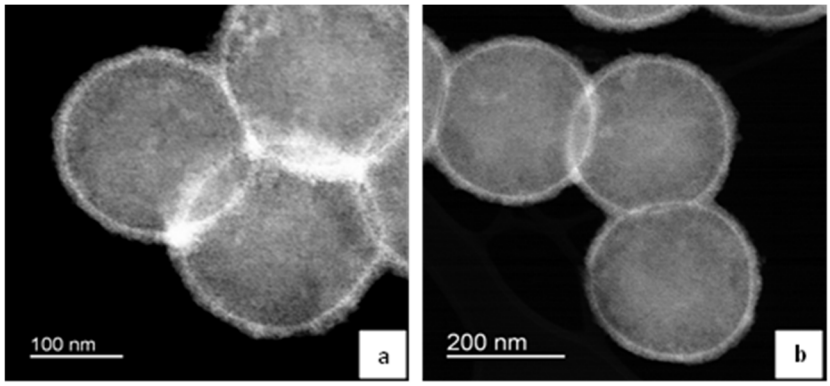

Figure 19. STEM micrographs of SiO_2@ZrO_2 oxide supports calcined at (a) 700°C and (b) 900°C.

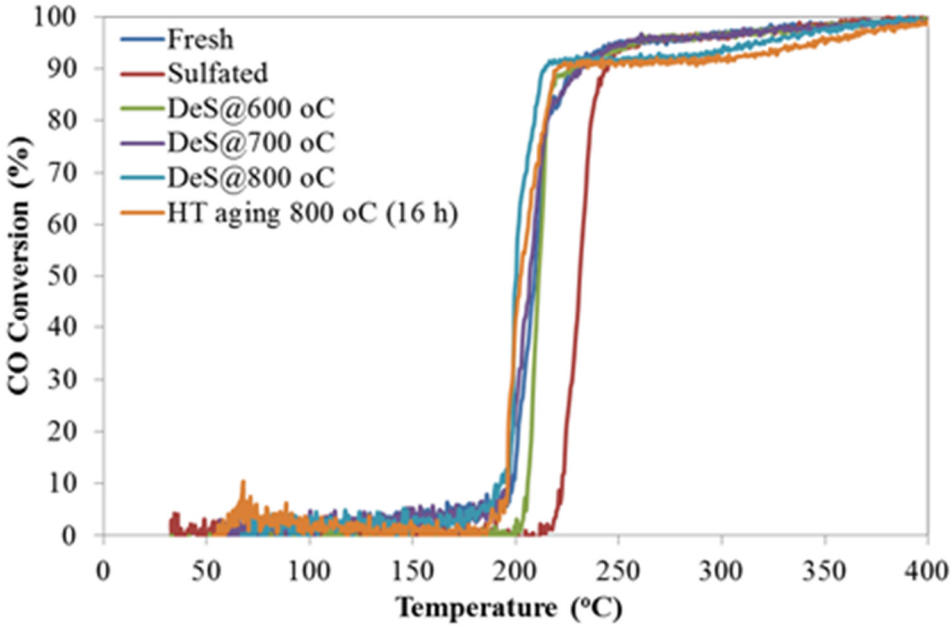

Figure 20. Catalytic performance of 2.5 wt% Pd/SiO_2@ZrO_2 in the oxidation of CO under lean conditions with a total flow rate of 200 ml/min (4000 ppm CO/1000 ppm C_3H_6/500 ppm NO+10% O_2 + 5% H_2O + Ar balance) for fresh, sulfated, desulfated at 600, 700 and 800°C and lean hydrothermally aged at 800°C (16 h) states.

Later, the catalyst material was exposed to stoichiometric aging conditions, and performance was evaluated under slightly rich conditions; the light-off behavior suffered greatly. After aging at 900°C with less than 0.05% O_2, the activity of 2.5 wt% Pd/SiO_2@ZrO_2 had such a significant loss that it was decided to abandon this approach. It can be seen in Figure 21 that the propane conversion never achieved 90%.

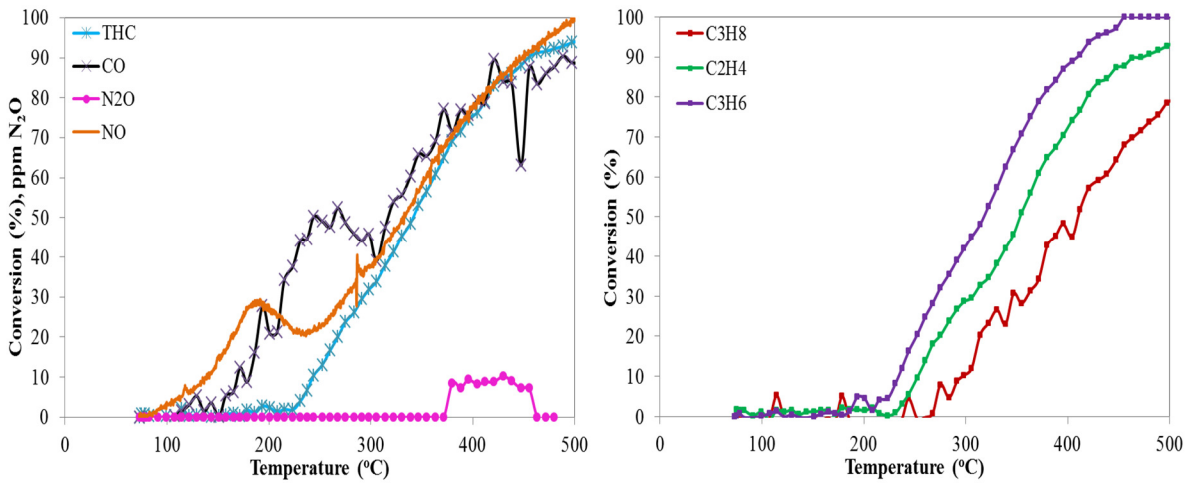

Figure 21. S-GDI (less 0.05% O_2) evaluation of 2.5 wt% Pd/[SiO_2@ZrO_2] aged at 900ºC.

2.3.3 Ternary Oxide Development as PGM Substitute

Excellent low temperature reactivity for CO oxidation was found with a precious metal-free ternary oxide mixture of Cu, Co, and Ce with light-off temperatures for CO below 100°C under lean conditions. Even after calcining at 800°C under lean conditions, the CO T90 continued to be below 200°C in the presence of HCs and NOx (Figure 22). However, the HC conversion was poor with T90s of approximately 400°C, so precious metals would still be required in a fully formulated catalyst.

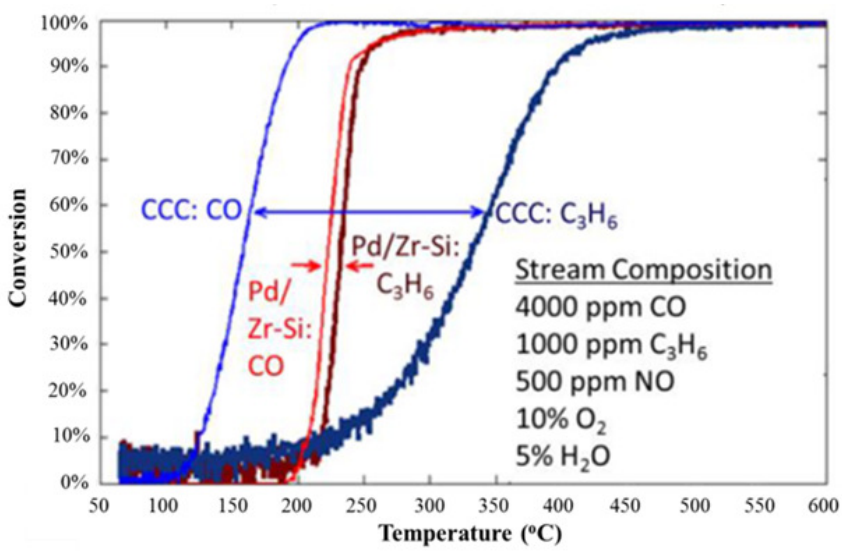

Figure 22. CO (thin/light) and C_3H_6 (thick/dark) light-off curves of CuOx-CoOy-CeO_2 (CCC) (blue) and PGM (red) catalysts in simulated exhaust conditions. Arrows highlight significant change in the response to propylene.

The synthesis route involved a co-precipitation technique utilizing $Cu(NO_3)_2$, $CoCl_2$, and $Ce(NO_3)_3$. This technique resulted in a catalyst with a metal molar ratio of 1:5:5 (Cu:Co:Ce), dubbed CCC. Figure 23 shows a representative EDX (electron dispersive X-ray) elemental mapping of the CCC catalyst for each of the relevant metals. Again, distinct regions of cobalt oxide and ceria were evident though there was considerable mixture of these distinct phases throughout. A copper signal could be seen throughout the sample with no particular bias toward either the Co_3O_4 or CeO_2 phases. Since no copper phase was seen via TEM or XRD, it was evident that the Cu component was embedded into the lattices of both Co_3O_4 and CeO_2 phases.

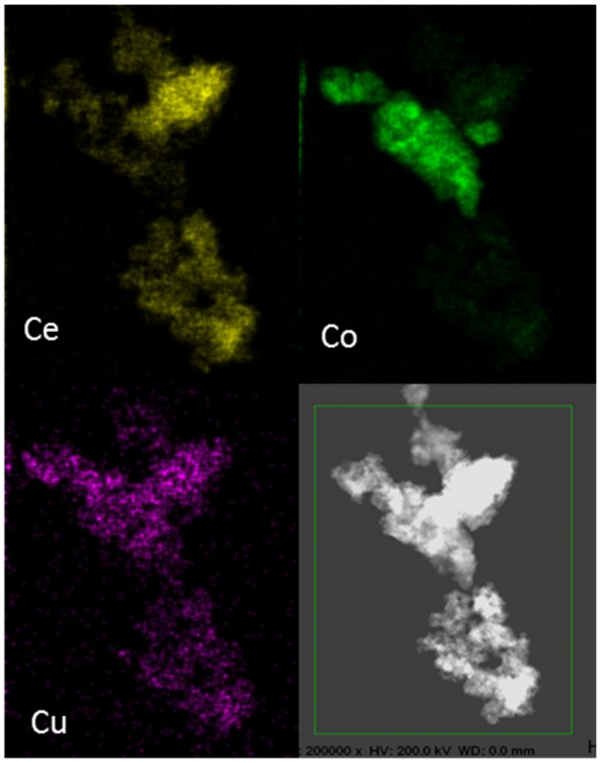

Figure 23. EDX elemental mapping of CCC catalyst particle. Cu signal was seen throughout both Co_3O_4 and CeO_2 regions.

Based on promising literature, a formulation of CCC which included a Mn component was synthesized. The molar ratio of Cu, Mn, Co, and Ce was 1:1:5:5, respectively. Chlorides were eliminated from the synthesis precursors due to industry concerns; no difference in activity was seen between samples synthesized with and without chlorides. Figure 24 shows the activity of this formulation, dubbed CMCC under both lean (LTC-D) and slightly rich (SGDI) conditions. The full effect of water on this catalyst under stoichiometric conditions was evaluated (Figure 25). Results showed that, as expected, water was a major inhibitor of these catalysts. H_2O content as low as 1% was enough to bring the catalyst to its final activity.

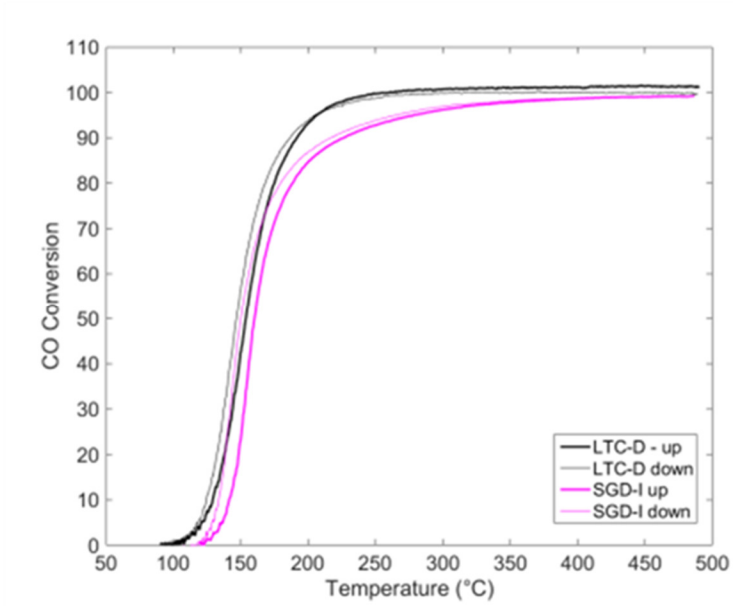

Figure 24. CMCC catalyst activity for CO under LTC-D (lean) and SGDI (rich) evaluation conditions.

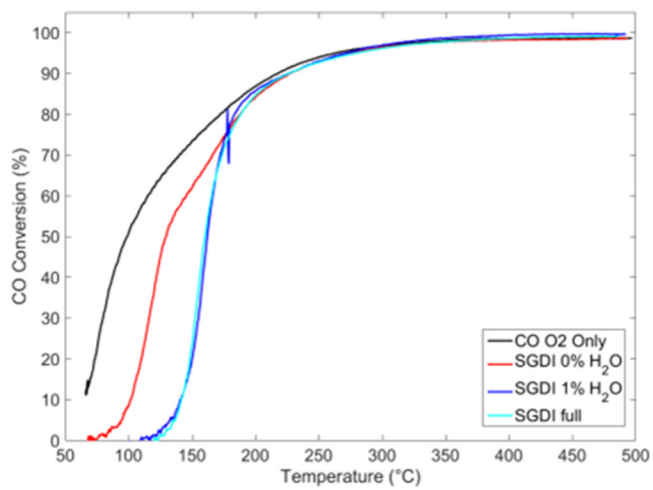

Figure 25. CMCC catalyst under varying water conditions to determine inhibition effects for CO activity.

It was determined that while the CCC and CMCC materials showed promise for low temperature conversion of CO after mild aging, harsher aging at higher temperatures severely degraded the performance. Sulfur poisoning and removal were additional issues. It was decided to stop work on this type of catalyst for gasoline (stoichiometric) engine applications.

2.3.4 Core@Shell Model Catalysts

In order to prove out the synthesis of core@shell model catalysts, silica was first used as a shell because the chemistry was known to be suitable to the planned techniques, even though silica (SiO_2) was known to lack sufficient durability for high temperature exhaust gas applications. A "microemulsions method" was used to prepare Pd@SiO_2 core@shell powders with different metal loadings. SiO_2 was formed as a shell around a Pd core to protect the active Pd site from contamination and thermal sintering that would cause loss in surface area. Micrographs obtained via Transmission Electron Microscopy (TEM) of Pd@SiO_2 particles with different loadings are shown in Figure 26. There appeared to be a relationship between metal loading and shell thickness. The particles in the sample with a nominal Pd loading of 4 wt% had a shell thickness of about 20 nm, while the sample with a lower Pd loading (0.4 wt%) had much thicker shells in the range of about 40 nm. CO conversions of 90% were found below 200°C for the 4 wt% Pd sample when it was fresh (Figure 27).

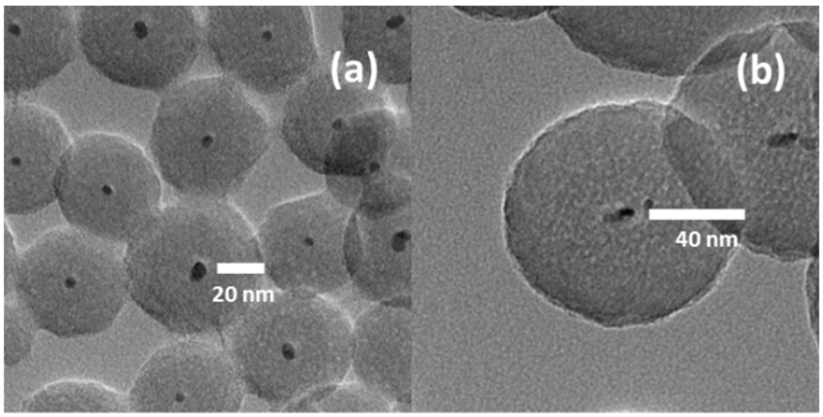

Figure 26. Electron micrographs of Pd@SiO_2 particles with different loadings. The left panel (a) presents a 4 wt% Pd loading, while the right panel (b) presents a 0.4 wt% Pd loading.

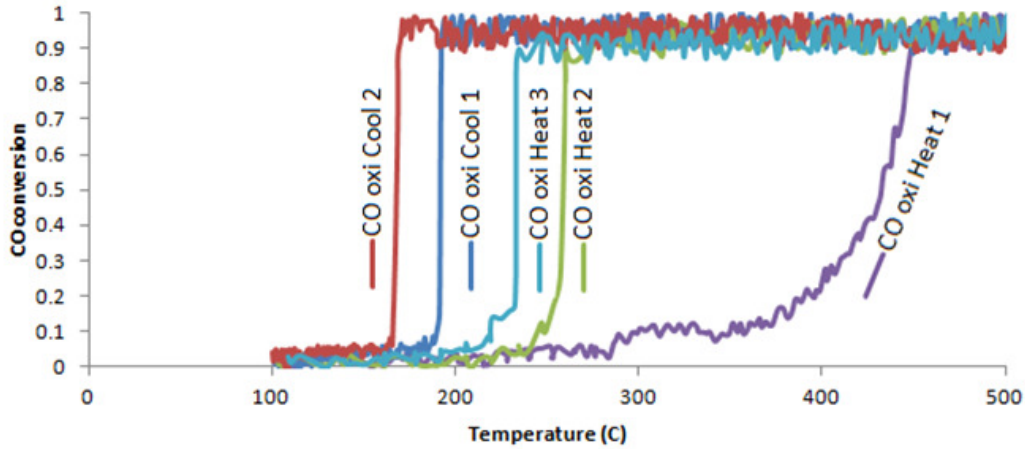

Figure 27. Multi-cycling CO oxidation test for fresh Pd@SiO_2 core@shell particles (4 wt% Pd). "Heat" designates a temperature ramp from low to high, and "cool" designates a temperature ramp from high to low.

A method was also developed to prepare active, more durable Pd@CeO_2 core@shell particles as shown schematically in Figure 28. Electron microscopy images are shown in Figure 29, where CeO_2 particles were observed on the surface of the particle.

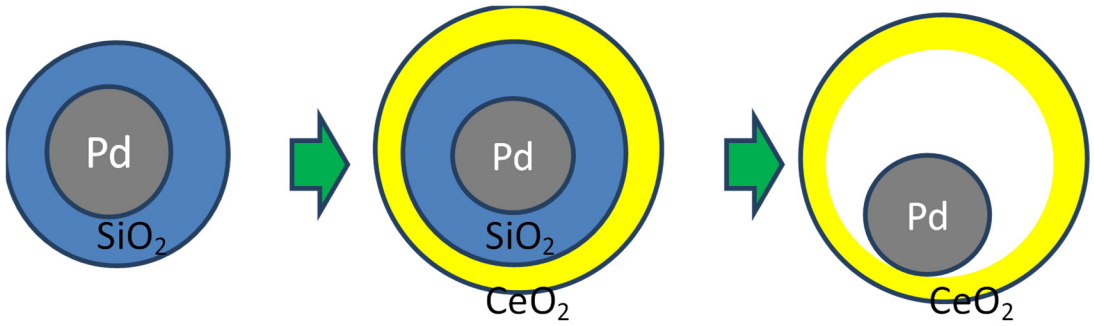

Figure 28. A new schematic for preparing core@shell nanoparticles with palladium core and an oxide material (CeO_2 for the first choice of material) other than silica.

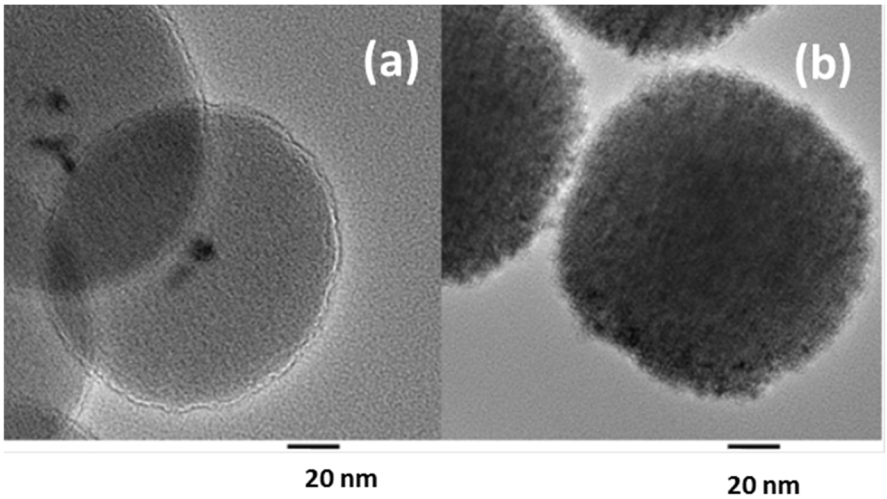

Figure 29. Electron micrographs of Pd@SiO_2@CeO_2 core@shell particles. The surface of Pd@SiO_2 (a) was coated with cerium oxide nanoparticles to produce Pd@SiO_2@CeO_2 particles (b). The scale bar represents 20 nm for both images.

A series of additional model catalysts, including Pd@CeO_2@ZrO_2 and Pd@CeO_2@ZrO_2 with Rh deposited on the outside were prepared to demonstrate the use of a metal core confined in a shell to prevent sintering, while at the same time lowering the light off temperature. As expected, switching from a SiO_2 to a CeO_2 shell brought a significant decrease in T90s for all reactants. Adding an additional ZrO_2 layer did not alter the activity by much, as the ZrO_2 layer was implemented to improve hydrothermal stability. In fact, the Pd@CeO_2@ZrO_2 catalyst performed slightly worse than the Pd@CeO_2 catalyst in the degreened state. Finally, decorating the exterior with Rh at low loading further improved the activity. The durability was tested by aging the model catalysts under the reaction stream at 800°C for 10 h. After aging, in general, the activity degraded as expected (Figure 30). However, catalysts with ZrO_2 double-shell were more hydrothermally stable than catalysts without, as the Pd@CeO_2@ZrO_2 catalyst performed better than Pd@CeO_2 after aging. This result confirms that application-specific core@shell catalysts can be designed and synthesized based on the properties needed for the application. While the demonstrated survival of core@shell structures during aging at 800°C is quite remarkable, there is still the challenge of making these types of catalysts survive temperature spikes up to 960°C or even 1000°C, meeting current and future automotive industry requirements.

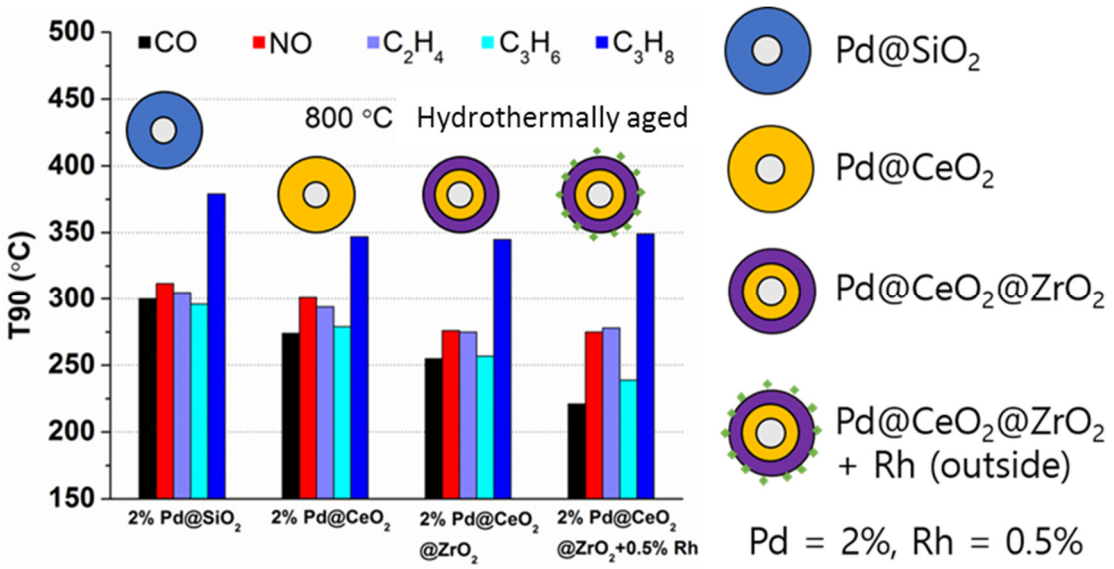

Figure 30. T90 performance of 800°C hydrothermally aged core@shell model catalysts using USCAR ACEC test protocols.

2.3.5 Methods for washcoating and deployment of core@shell catalysts

The amount of core@shell catalyst material generated in the project was significantly below the amount needed to coat a 1" x 1" monolith core; therefore, no washcoating methods specific to core@shell materials were pursued.

2.3.6 Cross Lab Characterization and Combined Materials Development

Cross-lab reactor comparison of commercial TWC activity was comparable and demonstrated similar temperatures for 50% conversion of various chemical species typically present in gasoline engine exhaust (HC, CO, NOx). This was described in an earlier section (Task 2.2).

The team confirmed several supported metal catalyst structures made in this program to promote lower light-off temperatures, enhance metal-support interactions, and improve durability. Electron microscopy was conducted using the 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) at ORNL (Figure 31). Ford was able to confirm the overlayer geometry with well dispersed Ti and Rh. Similar structural confirmation was completed on ORNL's deposition of Pd on Ce-Zr nanoparticles onto an alumina support using a strong electrostatic adsorption method. Images were also obtained of hollow @zirconia sphere that could be used to support precious metals. The UM team succeeded in developing a one-pot synthesis method for core@shell catalysts.

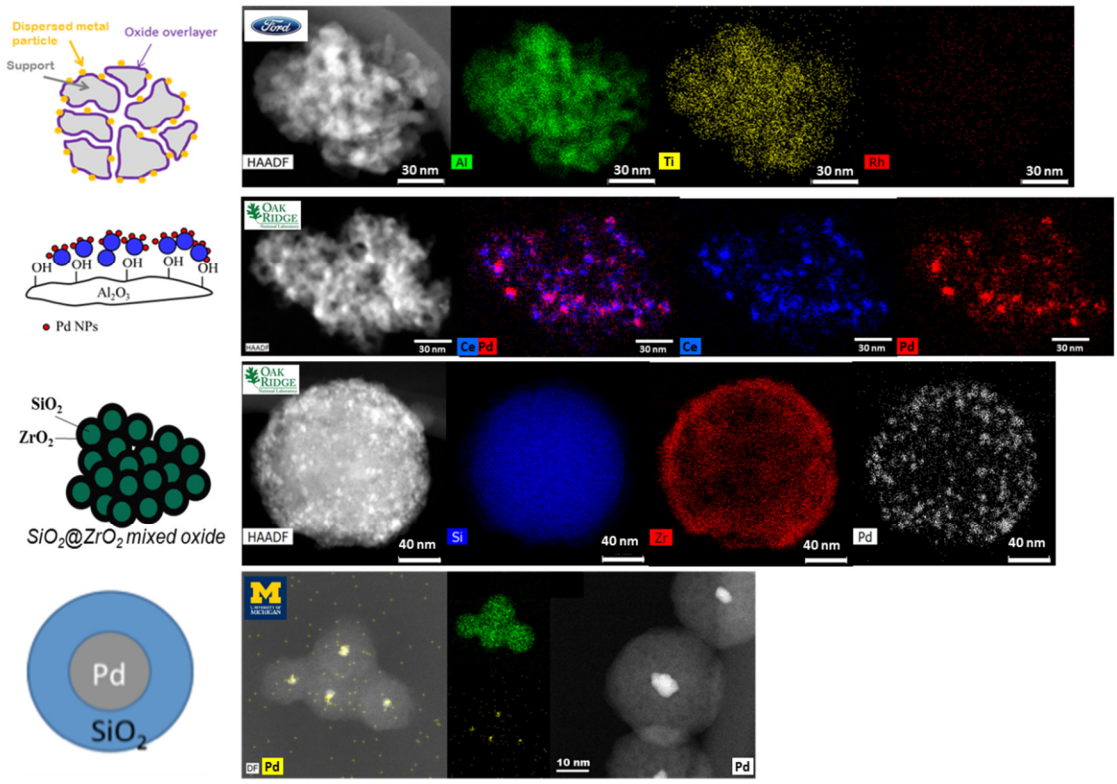

Figure 31. Confirmation of catalyst structures using the Talos electron microscope at Oak Ridge National Laboratory.

3 COMPUTATIONAL MODEL EVALUATION

Calibration of internal models with kinetics measured over the 0.5% Rh on 8% Ti-overlayered Al_2O_3 light-off catalyst was continued. Rate parameters for oxidation of CO, water-gas shift, and oxidation and steam reforming of propane were measured in the laboratory and transferred to the model. While the resulting model could accurately describe conversion of CO-propane mixtures, the results were not transferrable to more complex reaction mixtures: interference effects among multiple species significantly altered the kinetics of each species from the results obtained when species were evaluated separately. Development of a multi-species kinetic model capable of accounting for this complexity was projected to greatly exceed the time available for modeling tasks for this project. Modeling using lumped rate equations calibrated against experimental reference data resulted in an estimate of 10-15% reduction in tailpipe NMOG + NOx on the Federal Test Procedure for light-duty vehicles.

4 CATALYST SYSTEM COST MODEL

Discussions were held with suppliers on processing cost directions and opportunities regarding sourcing of stabilized alumina, and incorporation of titania or zirconia overlayers. Already-commercialized versions of Si-stabilized were identified as lower cost alternatives to the processing techniques used in this project. Opportunities to alter synthesis procedures to eliminate the need for a milling step, thereby further reducing manufacturing costs and streamlining production, were also investigated. Although the precious metal usage of the 0.5% Rh catalyst is less than 1/3 of a commercial catalyst at 1.7% Pd, the cost of the additional manufacturing step is unknown at this time. The estimated precious metal costs for a 2L catalyst containing one or two layers is included in Table 3. The costs were estimated using precious metal pricing available on kitco.com in November of 2017. The $Rh/Ti/Al_2O_3$ catalyst would be significantly less cost than a production TWC via the use of less metal loading; however, adding a layer of oxygen storage capacity (OSC) material containing Pd and ceria/zirconia would increase the cost up to and including parity with the commercial sample, albeit at much higher performance. Rhodium is the least abundant of the three precious metals (Pt, Pd, and Rh) used in automotive catalysts today, and widespread Rh usage at the levels used in these experimental materials would most likely result in significantly higher Rh prices relative to today's market price.

Table 3.
Estimated precious metal costs for a 2L catalyst containing one or two layers.

Catalyst	**Pt:Pd:Rh (g/ft^3)**	**PGM Cost (2 L cat)**
Production TWC	0:78:2	$180
Rh/Ti light-off	0:0:25	$70
Rh/Ti light-off + low OSC	0:0:25 + 0:23:2	$125
Rh/Ti light-off + high OSC	0:0:25 + 0:46:4	$180

Table 4.
Precious metal costs used in estimating full size catalyst costs.

Precious metal costs (kitco.com 11/7/17)			
	Pt	Pd	Rh
Per troy oz	$920	$988	$1195
Per gram	$28.58	$31.77	$38.42

5 PROTOTYPE SYSTEM DEVELOPMENT, DEMONSTRATION AND EVALUATION

Ford, ORNL, and UM worked with a major catalyst supplier (Johnson Matthey) to transfer the down-selected catalyst materials and synthesis procedure for the catalysts. This involved iterations on procedure modifications to ensure scale-up capability and verification of any scale-up effects. The goal was to verify activity on a ceramic honeycomb monolith tested in the reactor and compared to the original catalyst powder sample.

5.1 Washcoat Scale-up

A sample of 0.5 wt% Rh on 8 wt% titanium on Al_2O_3 milled to ca. 10 microns was sent to Johnson Matthey. The material was coated onto a ceramic honeycomb monolith core as part of the scale up effort and sent back to Ford for testing. The degreened 1" diameter core sample was tested with the USCAR ACEC protocol (Figure 32). The results were comparable to the high performing powder sample with the same composition.

Ford prepared a similar ceramic honeycomb monolithic core sample but with a different, stepwise preparation procedure. First, Al_2O_3 particles were added to the monolith by repeated cycles of coating and calcination to obtain a total loading of 1 g. Then approximately 5 wt% TI was added to the Al_2O_3 via the previously described alkoxide hydrolysis method, followed by another calcination. Finally, 0.5 wt% Rh was deposited onto the titanium oxide overlayer, followed by another calcination. The degreened reactor results produced the lowest T90s of any material in this project (Figure 33).

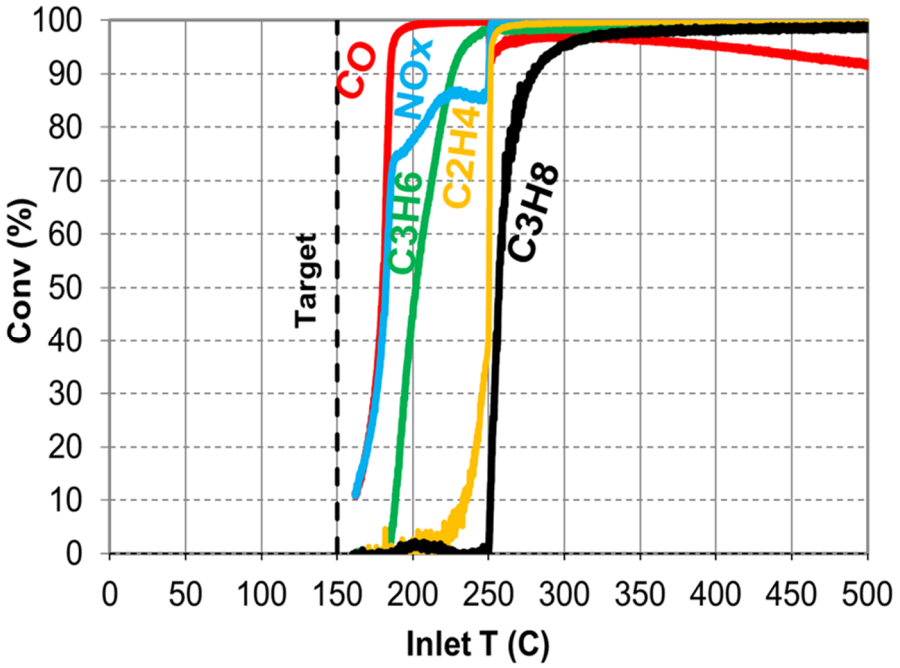

Figure 32. Ceramic honeycomb monolith sample coated by Johnson Matthey that incorporates the active catalyst $Rh/Ti/Al_2O_3$. Reactor results are for a degreened sample. Geometric space velocity was 30,000 h^{-1}.

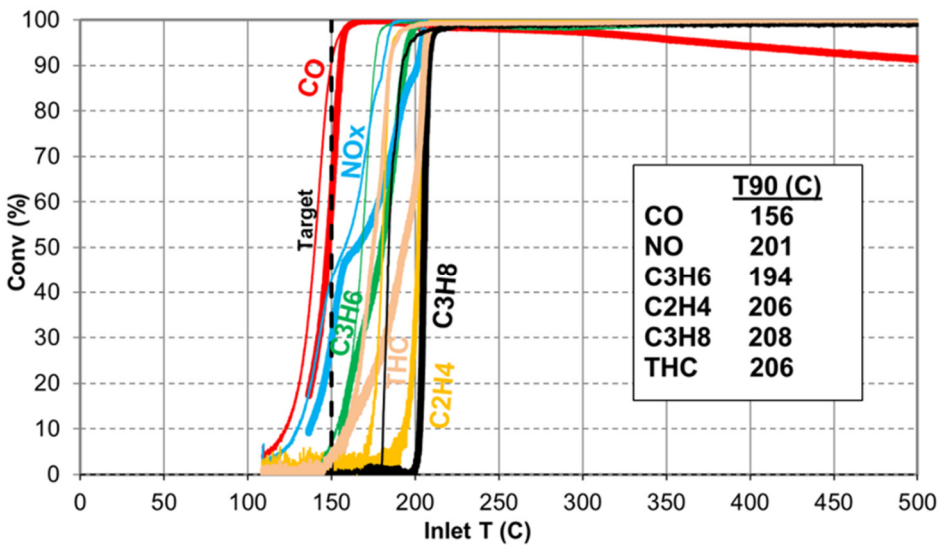

Figure 33. Ceramic honeycomb monolith sample coated at Ford that incorporates the active catalyst $Rh/Ti/Al_2O_3$. Reactor results are for a degreened sample. Geometric space velocity was 30,000 h^{-1}.

5.2 Improve BP2 Methods for wash coating and deployment of core-shell catalysts

The amount of core@shell material produced was too small for coating a small ceramic monolith for reactor testing; therefore no activity was performed under this task.

5.3 System Integration

A TWC functioning in a real exhaust system contains oxygen storage material to better handle the fluctuations in air/fuel ratio that come with transient vehicle operation. The Pd/nano-CZO/Al_2O_3 material contained some oxygen storage capacity; it was decided to test the light-off behavior of that material combined with $Rh/Ti/Al_2O_3$.

A 50/50 uniform physical mixture of Rh-Ti-Al_2O_3 and Pd-CZO was evaluated under the same test conditions. T90s for CO, NO, and propane were 205°C, 231°C, and 277°C respectively, as shown in Figure 34. The physical mixture of half Rh-Ti-Al_2O_3 and half Pd-CZO yielded lower T90s for all species than either material alone. Evidently a favorable synergy exists when these formulations are combined.

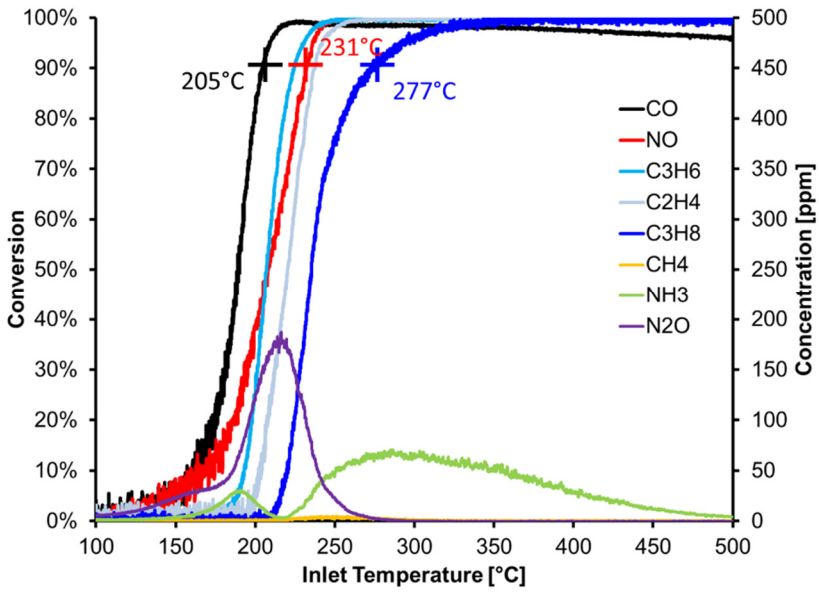

Figure 34. Degreened light-off performance of a physical mixture of 0.3 g of 0.5 wt% Rh on 8 wt% Ti/Al_2O_3 and 0.3 g of 2 wt% Pd on nano-CZO/Al_2O_3. T90s for CO, NO, and propane were 205°C, 231°C, and 277°C respectively.

CONCLUSIONS

Three-way catalyst (TWC) activity at low temperatures was improved significantly compared to a commercial sample after simulated high mileage aging. While the ultimate goal of 90% conversion at 150°C was not achieved for all of the chemical species tested, the downselected program materials (Rh/Ti/Al_2O_3, Rh/Zr/Al_2O_3, Pd/nano-CZO/Al_2O_3, Pt/nano-CZO/Al_2O_3) had T90s that were up to 128°C lower. These materials survived stoichiometric and/or four mode aging at 900-960°C peak temperatures. The best Rh version containing Ti overlayer had the lowest aged T90 for CO of 190°C, and was scaled up to a monolith core with favorable degreened results.

It was determined that while the base metal CCC and CMCC materials showed promise for low temperature conversion of CO after mild aging, harsher aging at higher temperatures severely degraded the performance. While the demonstrated survival of core@shell structures during aging at hydrothermal 800°C is quite remarkable, there is still the challenge of making these types of catalysts survive temperature spikes up to 960°C or even 1000°C, meeting current and future automotive industry requirements. Materials must also survive stoichiometric and rich conditions at high temperatures. The amount of core@shell catalyst material generated in the project was significantly below the amount needed to coat a 1” x 1” monolith core; therefore, no washcoating methods specific to core@shell materials were pursued.

RECOMMENDATIONS

Future research efforts should be directed in the following areas:

Scaled-up cores need to be evaluated after simulated high mileage aging. Work should continue with both catalyst coaters and material suppliers to develop cost effective methods of producing the most promising catalyst materials and coating them onto ceramic monoliths. The low light-off materials need to be combined with low temperature oxygen storage materials to gain the full three-way benefit during transient vehicle operation with modulating air/fuel ratio. The high temperature durability will remain important given the downsizing of boosted gasoline engines now and in the future for higher fuel economy. The low light-off materials should also be considered for hybridized vehicles with an internal combustion engine.

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PUBLICATIONS/PRESENTATIONS

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2. Chang Yup Seo, Eongyu Yi, Richard M. Laine, Galen B. Fisher, and Johannes W. Schwank, "Preparation of Palladium@Zirconia Core@Shell Nanoparticles Via Flame Spray Pyrolysis: A Potential Model Three-Way Catalyst", Michigan Catalysis Society Spring Symposium, Detroit, MI, May 13, 2015.
3. Andrew J. Binder, Todd J. Toops, Raymond R. Unocic, James E. Parks II, Sheng Dai, "Inhibition-Resistant Ternary Oxide Catalyst for Low Temperature CO Oxidation in Automotive Exhaust," 24th North American Catalysis Society Meeting (NAM), Pittsburgh, PA, June 18, 2015.
4. Mi-Young Kim, Eleni A. Kyriakidou, Jae-Soon Choi, Todd J. Toops, Cyril Thomas, Andrew Binder, James E. Parks II, Viviane Schwartz, Jihua Chen, "Impact of ZrO_2 on the Durability and Low-Temperature Performance of Pd-based Diesel Oxidation Catalysts," 24th North American Catalysis Society Meeting (NAM), Pittsburgh, PA, June 19, 2015.
5. (INVITED-Keynote) Todd J. Toops, James E. Parks, Eleni Kyriakidou, Andrew Binder, Jae-Soon Choi, Michael Lance, "Approaches to the challenges of treating emissions at low temperatures," Emissions 2015, Troy, MI, June 23, 2015.
6. Andrew J. Binder, Todd J. Toops, Raymond R. Unocic, James E. Parks II, Sheng Dai, "Inhibition-Resistant Ternary Oxide Catalyst for Low Temperature CO Oxidation in Automotive Exhaust," 14th Annual Fall Symposium of the Southeastern Catalysis Society, Clemson, SC, September 28, 2015.
7. Chang Yup Seo, Eongyu Yi, Richard M. Laine, Galen B. Fisher, and Johannes W. Schwank, "Preparation of a Palladium@Zirconia Core@Shell Nanopowder Catalyst Via Flame Spray Pyrolysis", AIChE 2015 Annual Meeting (ISBN: 978-0-8169-1094-6), Salt Lake City, Utah, Nov. 8-13, 2015.
8. (INVITED-Keynote) Todd J. Toops, James E. Parks, Eleni Kyriakidou, Andrew Binder, Jae-Soon Choi, Michael Lance, "Approaches to the challenges of treating emissions at low temperatures," PACIFICHEM, Honolulu, Hawaii, December 15, 2015.
9. C. Y. Seo, X. Chen, G. B. Fisher, M. Nahata, and J. Schwank, "Preparation of thermally stable Pd core@shell catalysts for CO oxidation", Michigan Catalysis Society 37th Annual Spring Symposium, Midland, MI, May 4, 2016.
10. Christine Lambert, DOE Annual Merit Review, June 2016.
11. Mi-Young Kim, Eleni A. Kyriakidou, Jae-Soon Choi, Todd J. Toops, Andrew J. Binder, Cyril Thomas, James E Parks II, Viviane Schwartz, Jihua Chen, Dale K. Hensley, "Enhancing Low-Temperature Activity and Durability of Pd-based Diesel Oxidation Catalysts Using ZrO_2 Supports," Applied Catalysis B 187 (2016) 181-194.
12. Joseph Theis, Andrew Getsoian, Christine Lambert, "The development of low temperature three-way catalysts for high efficiency gasoline engines of the future", SAE 2017-01-0942.
13. Christine Lambert, DOE Annual Merit Review, June 2017.
14. Chang Yup Seo, Eongyu Yi, Mohit Nahata, Richard M. Laine, Johannes W. Schwank, "Facile, one-pot synthesis of Pd@CeO_2 core@shell nanoparticles in aqueous environment by controlled hydrolysis of metalloorganic cerium precursor," Materials Letters 206 (2017) 105-108.
15. Eleni A. Kyriakidou, Todd J. Toops, Michael J. Lance, Jae-Soon Choi, James E. Parks II, "Advanced support modifications to improve the low-temperature activity and durability of Pd-based emissions control catalysts," 25th North American Catalysis Society Meeting, Denver, CO, June 4-9, 2017.

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PATENT APPLICATIONS/INVENTIONS

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