

The Development of Low Temperature Three-Way Catalysts for High Efficiency Gasoline Engines of the Future

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ABSTRACT

In anticipation that future gasoline engines will have improved fuel efficiency and therefore lower exhaust temperatures during low load operation, a project was initiated in 2014 to develop three-way catalysts (TWC) with improved activity at lower temperatures while maintaining the durability of current TWCs. This project is a collaboration between Ford Motor Company, Oak Ridge National Laboratory, and the University of Michigan and is funded by the U.S. Department of Energy. The ultimate goal is to show progress towards the USDRIVE goal of 90% conversion of hydrocarbons (HC), carbon monoxide (CO), and nitrogen oxides (NO_x) at 150°C after high mileage aging. A reactor was set up at Ford to follow the catalyst testing protocols established by the USDRIVE ACEC tech team for evaluating catalysts for stoichiometric gasoline direct-injection (S-GDI) engines; this protocol specifies a stoichiometric blend of CO/H_2 , NO , C_3H_6 , C_2H_4 , C_3H_8 , O_2 , H_2O , and CO_2 for the evaluations. This paper summarizes some of the lessons learned from the reactor testing at Ford and also discusses the results on some initial catalyst formulations at Ford that consisted of palladium (Pd) on various oxide supports. The temperature ramp rate had little effect on the lightoff performance, but the O_2 level around stoichiometry and interactions between the gas species were found to significantly affect the light off temperatures. Al_2O_3 and ZrO_2 catalysts with 2% Pd were fairly robust to lean aging at 1000°C, but a TiO_2 powder with 2% Pd suffered significant degradation after lean aging at only 800°C.

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INTRODUCTION

Modern three-way catalysts (TWC) typically become active for the conversion of hydrocarbons (HC), carbon monoxide (CO), and the oxides of nitrogen ($\text{NO}+\text{NO}_2$, or NO_x) at temperatures near 300°C [1]. Therefore, they are very effective for catalyzing the removal of the HC, CO, and NO_x emissions from the current generation of gasoline-powered vehicles, which typically produce exhaust temperatures of 400 to 500°C during low load operation once the vehicle is warmed up. In addition to high catalytic activity, the TWC has been optimized for thermal durability so it can withstand very high catalyst bed temperatures (e.g., 1000°C) that can be generated during high load operation. With a combination of advanced TWC formulations, sophisticated control systems that control the air/fuel (A/F) ratio tightly around stoichiometry, and accelerated heating strategies to warm the TWC quickly during a cold start, auto manufacturers have been able to certify vehicles to very strict emission standards established by the US Environmental Protection Agency (EPA) and the California Air Resources Board (ARB).

In August 2012, the federal government issued new rules that would increase the average fuel economy of new vehicles to 54.5 miles per gallon (MPG) by 2025 [2]. These new fuel economy standards are expected to drive significant improvements in gasoline engine efficiency, particularly during low load operation. As a result, there will be less energy available for the exhaust, and the exhaust temperatures will drop significantly from the levels of today.

However, because of the increasing use of down-sized direct-injected gasoline engines and turbo-charging to improve fuel economy, the exhaust temperatures are expected to remain the same or even increase during high load operation. As a result, it is critical that the low temperature activity of the TWC be improved significantly while maintaining the thermal durability of today's TWC.

Recognizing the need for emission control systems with lower temperature activity for future, more efficient engines, the USCAR organization arranged a workshop in November 2012 with approximately fifty representatives from the automotive industry, emission control system and component suppliers, government agencies, universities, and national laboratories. From this workshop, the challenge was issued to develop exhaust catalysts with 90% conversion of HC, CO, and NO_x at 150°C after aging for the equivalent of the full useful life (FUL) on a vehicle, thus producing the so-called "150°C Challenge" [3].

In early 2014, the Department of Energy issued a Funding Opportunity Announcement (FOA) on behalf of the Vehicle Technology Office (VTO). One of the proposed areas of research was the development of High Performance Low Temperature Catalysts for Exhaust Aftertreatment. A joint proposal from Ford Motor Company, Oak Ridge National Lab (ORNL), and the University of Michigan (UM) was submitted for this area of research and in August 2014 the team was granted a three year award. This team, led by Ford, took on

the “150°C Challenge” by proposing a stoichiometric catalyst material discovery project to directly address anticipated lower temperature exhaust from gasoline vehicles beyond 2025.

The three partners are pursuing different types of catalysts and catalyst architectures in the program. Ford Motor Company is investigating different types of precious metal on various oxide supports, Oak Ridge National Lab is pursuing base metal catalysts and precious metal catalysts on modified silica, and the University of Michigan is developing core-shell catalysts with different types of precious metal. The intent is to integrate the best developments from the three organizations into the final catalyst. During the development, all three organizations are utilizing the catalyst testing protocols for stoichiometric direct-injection gasoline (S-GDI) engines developed by the Advanced Combustion and Emission Control (ACEC) tech team of the USDRIVE organization [4].

Progress toward development of new catalyst materials capable of meeting the “150°C challenge” has been guided by two principles: (1) precious metals other than palladium (Pd), platinum (Pt), and rhodium (Rh) are generally not suitable for use in automotive environments [1], and therefore improved low temperature performance will require extracting greater activity from the precious metals already used in modern TWCs; and (2) the activity of a precious metal can be improved by tuning its interaction with the oxide support onto which it is deposited [5]. The initial materials development at Ford concentrated on identifying support oxides that could improve the activity of the precious metal relative to the conventional alumina (Al_2O_3) support. Specifically, catalysts consisting of Pd on pure titania (TiO_2), pure zirconia (ZrO_2), and pure Al_2O_3 were prepared and evaluated in this work. Catalysts containing alternative precious metals (e.g., Rh), and/or mixtures of support oxides that can improve the thermal durability of the catalyst are also being pursued in the project and will be presented in a future publication.

The intent of this paper is to discuss the initial catalyst formulations developed at Ford and the lessons learned from the reactor testing, including the effects of the temperature ramp rate, the air/fuel (A/F) ratio (i.e., O_2 level) near stoichiometry, and the interactions (positive and negative) between the different exhaust species. This paper also presents an initial look at the thermal durability of the catalysts.

EXPERIMENTAL

Catalysts

Early in the project, it was desired to establish a correlation between the powder reactors at Ford, ORNL, and UM by testing samples of the same catalyst. A production TWC was tested on the monolithic reactor at Ford, ground into powder, and retested on the powder reactor. Samples of the powder were then sent to ORNL and UM for evaluation on the reactors at those facilities. The monolithic catalyst was a production TWC containing oxygen storage materials and a loading of 6.9 g/L (196 g/ft³) Pd and 0.14 g/L (4 g/ft³) Rh; no further details on the formulation will be provided out of respect for the supplier. This sample had been aged for 50 hours on a pulse-flame combustion reactor [6] using the Ford 4-mode durability cycle, where

the inlet temperature was 850°C and the A/F ratio cycled each minute between 40 s of stoichiometric operation, 6 s of rich pulsator operation with 4% CO, 10 s of rich pulsator operation with air injection in front of the catalyst (3% CO + 3% O_2) to produce a large exotherm, and 4 s of lean pulsator operation (3% excess O_2). The peak catalyst bed temperature on this schedule was ca. 960°C. This aging schedule is accepted by the U.S. Environmental Protection Agency as a rapid and cost-effective method of producing catalysts that reflect high mileage aging on a vehicle.

The experimental catalysts developed at the three facilities were in the form of catalyst powders, with the intention that the best candidates would be coated onto monoliths for laboratory and engine testing during the final year of the project. At Ford, a sol-gel process [7] was used to prepare approximately 15 g batches of alumina (Al_2O_3), titania (TiO_2), or zirconia (ZrO_2) from precursors of aluminum butoxide, titanium butoxide, or zirconium butoxide, respectively. The appropriate amount of the butoxide was mixed with deionized water and nitric acid in a molar ratio of 1:100:0.07, covered with aluminum foil, and stirred overnight on a hot plate to complete the peptizing. For most of the catalysts, a measured amount of Pd ammine nitrate was added directly to the wet sol; this method of precious metal addition is often referred to as a “catalyzed slurry” or “one-pot” technique. The foil was removed, and the Pd-containing sol was allowed to boil down to a gel. The gel was dried overnight at 110°C and then calcined in air at 550°C for approximately one hour. While most of the catalysts were prepared with this catalyzed slurry synthesis technique, in a few cases the alumina, zirconia, or titania washcoat powder was prepared with the sol-gel process, dried and calcined, impregnated with the Pd precursor, and then dried and calcined again. This method of PGM addition is commonly referred to as the “post-impregnation” (PI) technique [8]. The preparation of both catalyzed slurry and post-impregnated catalysts with the same washcoat was intended to explore the effect that the technique of precious metal addition had on the catalytic performance. The catalyst powders were crushed and sieved to a size of 500 to 850 μm prior to surface area measurements and reactor testing.

As an initial assessment of the thermal durability of the catalysts, samples of the powders were oven aged in air with 10% H_2O for 4 h at 800, 900, or 1000°C. The fresh and aged catalysts were assessed for BET surface areas with N_2 adsorption using a Micromeritics ASAP 2420 Surface Area and Porosity Analyzer.

Reactor Testing

The reactor used in this project at Ford had the capability to test catalyst powders as well as monolithic core samples. For the monolith tests, a 2.54 cm by 2.54 cm core sample was wrapped with non-intumescent mat material and inserted into a quartz tube, and the tube was placed inside a horizontal furnace with programmable temperature controls. The oven thermocouple outside of the quartz tube was used to control the oven, and a type K thermocouple was inserted into the rear face of the monolith sample to a depth of ca. 1 cm for measuring and recording the bed temperature. The flow rate was held at 6.4 L/min, resulting in a space velocity of 100,000 h⁻¹. The 2.54 cm x 2.54 cm monolithic core sample.

For the powder testing, a vertical furnace was used with a quartz reactor containing two concentric tubes with countercurrent flow (referred to as a “tube within a tube”). As shown in Figure 1, approximately 2 g of the catalyst powder was placed on the porous glass frit within the inner tube (diameter of ca. 2.54 cm). This amount of catalyst corresponded to the amount of washcoat on a 2.54 cm by 2.54 cm monolith sample, assuming a washcoat loading of 0.15 g/mL (2.5 g/in³). So with the flow rate of 6.4 L/min, the effective space velocity remained at 30,000 h⁻¹. The exhaust gas entered the glass reactor through the top side arm where it was then directed in a downward direction through the inner tube. The exhaust passed through the catalyst powder and the frit and then passed in an upward direction in the space between the inner tube and the outer tube and then out the bottom side arm. A single type K thermocouple located approximately 2 cm above the powder bed was used to measure and record the inlet temperature and to provide feedback to the furnace controller. The exhaust from the monolithic reactor or the powder reactor was directed into a 1 Hz MKS Fourier Transform Infrared (FTIR) analyzer equipped with an inlet sample line heated to 191°C. To avoid H₂O condensation in the unheated lines downstream of the FTIR, the exhaust from the FTIR was diluted with N₂ before being passed to the ventilation system.

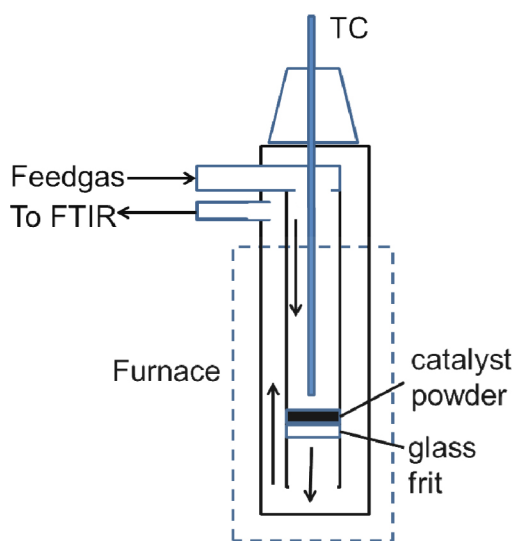


Figure 1. Glass apparatus for testing catalyst powders.

For both the monolithic reactor and powder reactor, the gas composition closely followed the catalyst testing protocols for stoichiometric gasoline engines that were established by the ACEC tech-team of USDRIVE [4]. This protocol specifies a stoichiometric mixture of C₃H₈, C₃H₆, C₂H₄, NO, CO/H₂, O₂, H₂O, and CO₂ for evaluating catalysts intended for gasoline engines operating at stoichiometry. Table 1 displays the concentration of the different exhaust species used at Ford. The concentrations of the three hydrocarbons were chosen to provide a total of 3000 ppm on a C1 basis. The CO and H₂ were supplied from the same bottle and were always in a 3:1 ratio. The protocol calls for CO₂ and H₂O concentrations of 13% to reflect the approximate levels of these species on a gasoline engine operating at stoichiometry; in this work, 10% CO₂ and H₂O were used. The protocol calls for 0.74% O₂ to provide a stoichiometric air/fuel (A/F) ratio; in this work, many of the tests were performed with 0.69% O₂ to provide a slight rich bias in

order to better simulate the average A/F ratio used on vehicles today. Also, the ACEC protocol specifies a temperature ramp rate of 2°C/min to produce essentially steady-state conversion vs temperature data. This ramp rate was also chosen out of consideration for facilities with analytical techniques that have significant time requirements, such as gas chromatography. In this project, the effect of the ramp rate on the conversion performance was evaluated early in the program. Based on this work, a ramp rate of 5°C/min was typically used during this project to increase the number of tests that could be performed in a day.

Table 1. Gas concentrations used during reactor testing at Ford.

Species	Concentration
C ₂ H ₄	525 ppm
C ₃ H ₆	500 ppm
C ₃ H ₈	150 ppm
NO	1000 ppm
CO/H ₂	5000/1667 ppm
O ₂	0.69% – 0.84%
H ₂ O	10%
CO ₂	10%
N ₂	Balance

In addition to the tests with the full gas mixture listed in Table 1, additional tests were performed with some of the gas species removed in order to evaluate the interactions (positive or negative) between the gas species. Tests were performed with the three hydrocarbons only, CO/H₂ only, the three hydrocarbons with NO, CO/H₂ with NO, or the three hydrocarbons with CO/H₂. For all of the different gas compositions, the H₂O and CO₂ concentrations remained at 10%, and the O₂ level was adjusted to provide a slight rich bias.

Finally, to study the effect of the O₂ level near stoichiometry on the catalytic performance, an Al₂O₃ catalyst with 2% Pd prepared by the catalyzed slurry technique was aged for 50 h at 950°C in air with 10% H₂O. The catalyst was then evaluated on multiple ramp tests with the full gas mixture in Table 1 but with O₂ levels of 0.69% (slightly rich), 0.74% (stoichiometric), 0.79% (slightly lean), and 0.84% (lean).

RESULTS AND DISCUSSION

Temperature Ramp Rate

The effect of the temperature ramp rate was assessed using the aged monolithic TWC described earlier. The catalyst was evaluated on the reactor during increasing and decreasing temperature ramps with ramp rates of 2, 3, 4, 5, and 10°C/min and using the full mixture of gases in Table 1. As an example, Figure 2 shows the conversion vs bed temperature data during the increasing and decreasing ramps on the aged TWC with a ramp rate of 5°C/min. For all five gas species (i.e., CO, C₃H₆, NO, C₂H₄, and C₃H₈), there was good agreement in conversion between the increasing ramp (thick lines) and the decreasing ramp (thin lines). The CO conversion exhibits a slight decline at higher temperatures due to the slight rich bias that was used. The catalyst reached high activity for converting the different gas species in the following order:

CO > C₃H₆ > NO > C₂H₄ > C₃H₈.