

Gasoline Cold Start Concept (gCSC™) Technology for Low Temperature Emission Control

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ABSTRACT

Stricter emission standards in the near future require not only a high conversion efficiency of the toxic air pollutants but also a substantial reduction of the greenhouse gases from automotive exhaust. Advanced engines with improved fuel efficiency can reduce the greenhouse gas emissions; their exhaust temperature is, however, also low. This consequently poses significant challenges to the emission control system demanding the catalysts to function at low temperatures both during the cold start period and under the normal engine operation conditions. In this paper, we will introduce a gasoline Cold Start Concept (gCSC™) technology developed for advanced stoichiometric-burn gasoline engines to meet future stringent emission regulations.

To improve the low temperature performance of three-way catalysts, a novel $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ mixed oxide was developed. Compared to conventional $\text{CeO}_2/\text{ZrO}_2$ mixed oxides with similar compositions, the new material exhibits higher oxygen storage capacity especially at low temperatures and is more thermally durable. The improved thermal stability of the new material further stabilizes and improves the PGM dispersion on the support. As a result, low temperature TWCs based on the new material exhibit a reduced light-off temperature. The improvement becomes obvious when the catalysts are tested on a vehicle with low exhaust temperatures.

For cold start HC emission control, HC storage components were further improved to increase the HC trapping capacity and HC release temperature. An emission control system combining the improved low temperature TWC and the enhanced HC trapping components demonstrates a noticeable reduction in the tailpipe emissions.

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INTRODUCTION

Three-Way Catalysts (TWCs) have been widely applied on stoichiometric-burn gasoline engine powered vehicles to reduce the tailpipe emissions of hydrocarbons (HC), carbon monoxide (CO) and nitrogen oxides (NOx). A conventional TWC can convert the three pollutants at nearly 100% conversion efficiency once it reaches its operation temperature, which is typically above 400 °C. Consequently, the majority of the tailpipe emissions are emitted under low temperature operating conditions of the vehicle, especially during the cold start periods. To reduce the cold start emissions, approaches such as placing the TWC in the close-coupled position and rapid warm-up engine control strategies are commonly adopted to quickly bring the catalyst to the operation temperature [1, 2, 3, 4, 5]. This does enable vehicles to meet the stringent government emission standards, but at the expense of their fuel economy.

A less commonly adopted technology to reduce the cold start emissions is HC traps. A typical HC trap consists of a zeolite and a TWC component. HC emissions are stored on the zeolite component during the cold start periods. As the exhaust temperature increases, the stored HC is passively released from the zeolite component and subsequently converted by the TWC component. So far, HC trap technology has seen only limited commercial applications [6, 7, 8, 9, 10]. A major technical hurdle is that, with the current HC traps, the HC release temperature is still relatively low compared to the light-off temperature of the TWC component. This limits the overall HC trapping capacity and conversion efficiency of the catalysts.

Starting in 2017 and beyond, together with the introduction of the next round of criteria pollutant tailpipe standards, US federal regulations also mandate a significant improvement in fuel economy and reduction of greenhouse gases (GHG) for light duty vehicles [1, 11]. While advanced engines and exhaust train systems with improved fuel efficiency can reduce CO₂

emission substantially, the exhaust temperature of these systems is expected to be much lower and can be below the normal operation temperature of a conventional TWC. This poses significant challenges to the emission control system, demanding the catalysts to function at low temperatures both during the cold start period and under normal engine operating conditions.

To address the challenges of low temperature emission control on stoichiometric-burn gasoline engine powered vehicles, a gasoline Cold Start Concept (gCSC™) technology has been developed and will be reported in this paper. This technology focuses on improving the low temperature performance of the TWC as well increasing the HC storage capacity and HC release temperature of the HC trap catalysts.

Many factors can influence the low temperature performance of a TWC. Among them, the nature of the support materials for the Platinum Group Metals (PGM) plays a critical role [2, 3, 4]. $\text{CeO}_2/\text{ZrO}_2$ mixed oxides have become an essential component in a TWC because of their unique oxygen storage and release properties. $\text{CeO}_2/\text{ZrO}_2$ mixed oxides not only enhance the intrinsic catalytic activity of the PGM components, but also provide Oxygen Storage Capacity (OSC) to the system minimizing the air/fuel ratio deviation from the stoichiometric point; both significantly improve the TWC performance of the system. Although most commercially available $\text{CeO}_2/\text{ZrO}_2$ mixed oxides exhibit excellent thermal stability, they lose their surface area considerably after high temperature exposure. As a result, even though a fresh TWC can exhibit excellent catalytic activity at temperatures below 400 °C, much of the low temperature performance is lost when the catalyst is aged to the end of its useful life. In this study, we developed a novel $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ mixed oxide that shows much improved thermal stability compared to a conventional $\text{CeO}_2/\text{ZrO}_2$ mixed oxide with a similar composition. In addition, the $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ mixed oxide exhibits higher OSC especially at low temperatures. With these improved properties, a TWC formulation based on the new material reduces the light-off temperature by nearly 50 °C.

Increasing the zeolite loading in a HC trap can increase the HC storage capacity [7]. At a given HC exposure level, higher HC storage capacity means lower HC coverage on the zeolite materials. This in turn improves HC trapping efficiency as well as increases HC release temperature. With conventional washcoated catalyst formulations, however, the zeolite loading can only be increased to a certain level because of the backpressure and processing constraints. To overcome the zeolite loading limitation, we utilize extruded zeolite substrates both as the support of the TWC component and as the HC storage component. Since the substrate body itself can contain a significant amount of zeolite materials, a high zeolite loading can be achieved with a minimum increase in backpressure.

Combining extruded zeolite substrates and low temperature TWC formulations enables us to increase the HC release temperature and to decrease the HC light-off temperature

simultaneously. This leads to the development of advanced HC trap catalysts with significantly improved net HC conversion efficiency. Such improvements will be demonstrated on a fuel efficient vehicle with low exhaust temperatures.

EXPERIMENTAL

Catalyst Preparation

A novel $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ mixed oxide was developed in house. The material was prepared by a co-precipitation method. Salts of cerium nitrate and zirconium nitrate were dissolved in water to form a mixed solution, which was subsequently mixed with $\gamma\text{-Al}_2\text{O}_3$ powder. By increasing the pH of the mixture, fine $\text{CeO}_2/\text{ZrO}_2$ mixed oxides were deposited on the alumina surface. The material was washed, dried, and finally calcined at 500 °C for 2 hours to form an $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ mixed oxide.

For comparison purposes, a conventional $\text{CeO}_2/\text{ZrO}_2$ mixed oxide was prepared following the same co-precipitation method without the addition of alumina powder. The resulting $\text{CeO}_2/\text{ZrO}_2$ mixed oxide was then blended with $\gamma\text{-Al}_2\text{O}_3$ powder to form a mixture of ($\text{Al}_2\text{O}_3 + \text{CeO}_2/\text{ZrO}_2$) that had an identical composition to the $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ mixed oxide.

Pd-loaded catalyst powders were made by impregnating Pd onto the $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ mixed oxide and the ($\text{Al}_2\text{O}_3 + \text{CeO}_2/\text{ZrO}_2$) mixture, respectively. The Pd loading was 1 wt.% in both samples.

Fully formulated TWC catalysts were prepared using the $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ mixed oxide and the ($\text{Al}_2\text{O}_3 + \text{CeO}_2/\text{ZrO}_2$) mixture, respectively, as the Pd support. A Rh component was also incorporated into the formulations. The exact PGM loadings, the substrate dimensions, and the TWC system configurations varied depending on how the catalysts were evaluated. The exact details will be specified in the next "results and discussion" section.

An advanced HC trap catalyst was made using an extruded zeolite substrate with 47 cells/cm² and a wall thickness of 280 μm (or 300 cpsi /11 mil). The zeolite loading in the substrate is about 4 g/in³. A low temperature TWC based on the $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ mixed oxide was directly coated on the extruded zeolite substrate. For comparison purposes, a conventional HC trap catalyst was made by washcoating a zeolite under-layer onto a ceramic substrate at a loading of 2 g/in³ of zeolite followed by a conventional TWC based on the ($\text{Al}_2\text{O}_3 + \text{CeO}_2/\text{ZrO}_2$) mixture on top of the zeolite layer.

Catalyst Aging, Characterization, and Evaluation

To assess their thermal stability, separate samples of both the $\text{Al}_2\text{O}_3/\text{CeO}_2/\text{ZrO}_2$ mixed oxide and the ($\text{Al}_2\text{O}_3 + \text{CeO}_2/\text{ZrO}_2$) mixture were calcined in air for 4 hours at 900, 1000, and 1100 °C, respectively. The pre-treated samples were then measured for specific surface area on a TCSAP 2420 from Micromeritics

Instrument. The crystalline phase of the calcined materials were analyzed by X-Ray Diffraction (XRD) using a PANalytical X'Pert PRO MPD diffractometer equipped with a programmable divergence slit, a programmable anti-scatter slit, a Ni filter, a PIXcel detector and a Cu K α source (45kV, 40mA). Hydrogen Temperature Programmed Reduction (H₂-TPR) experiments were conducted to measure the oxygen storage capacity (OSC) of the materials. Prior to the H₂-TPR experiments, the samples were pretreated at 500 °C in 5% O₂/He for 30 minutes. H₂-TPR was carried out in 5% H₂/He by heating the sample from 30 to 900 °C at 10 °C/min. The hydrogen consumption during the temperature ramp was monitored by a thermal conductivity detector.

The Pd loaded powder catalysts were redox aged at 1050 °C for 36 hours before the catalytic activity evaluation. The redox aging cycles were achieved by alternating the gas mixtures every 5 minutes between rich and lean as listed in [Table 1](#). The gas flow rate was kept at 3L/min and 20 ppm SO₂ was added in the feed gas during the aging. After aging, the powder catalysts were mixed with cordierite powders at a 1:4 ratio. The mixtures were loaded into tube reactors. Light-off activity of the catalysts was measured from 150 to 500 °C at a ramp rate of 10 °C/min in a feed of 1500 ppm C₃H₆, 400 ppm NO, 1% CO, 0.7% O₂, 10% H₂O, and N₂ balance. The redox aged powder catalysts were also analyzed by Transmission Electron Microscopy (TEM) to measure the Pd dispersion. The samples were embedded in resin and microtomed to 50nm thick slices. Compositional analysis was determined by X-ray emission detection in the scanning mode.

Table 1. 1050 °C/36h redox aging conditions

	CO (%)	O ₂ (%)	SO ₂ (ppm)	H ₂ O (%)	N ₂
Rich	0.5	-	20	10	balance
Lean	-	1	20	10	balance

Fully formulated TWCs based on the Al₂O₃/CeO₂/ZrO₂ mixed oxide were evaluated both on an engine dynamometer and on a fuel-efficient vehicle with low exhaust temperatures. For engine dynamometer evaluation, the catalysts were aged on a 4.6L engine using a 4-mode aging protocol with an average temperatures of 925 °C for 100 hours. Engine sweep tests on the aged catalysts were conducted at a space velocity (SV) of 112,000 hr⁻¹ with the air/fuel ratio increasing from 13.5 to 15.5 at a perturbation frequency of 1Hz and amplitude of 0.5. For vehicle evaluation, systems that consisted of a pair of close-coupled TWCs and a common underfloor TWC were aged on a 3.5L engine using a 4-mode aging protocol with an average temperature of 875 °C at the close-coupled locations. The aging time was selected to simulate the end of the useful life of the catalyst systems. The aged systems were evaluated on a fuel-efficient vehicle equipped with a 3.5L GTDI engine and a turbocharger.

A laboratory test was developed to assess the HC storage and release properties of the HC trap catalysts. Prior to the tests, the HC trap catalysts were aged at 800 °C for 80 hours in a flow of 5% H₂O in air. Each of the aged catalysts was pre-conditioned in the laboratory reactor at 650 °C for 5 minutes in a flow of 2250 ppm O₂, 10% H₂O, 10% CO₂, and N₂ balance to clean the HC storage sites before it was cooled to 80 °C. While the temperature was held at 80 °C, a mixture of propylene, iso-pentane, and toluene at a total concentration of 1500 ppm C₁ was introduced to the feed for 30 seconds to simulate the cold start conditions. This was followed by a rapid temperature ramp to 650 °C at a rate of 40 °C/min to simulate the warm-up period. During the temperature ramp, the HC concentration in the feed was reduced to 200 ppm C₁. During the test, the HC concentration in the outlet of the reactor was measured by a flame ionization detection instrument.

The HC trap catalysts were also tested on a fuel-efficient vehicle at the underfloor location in combination with a pair of close-coupled TWC catalyst to form a system. The aging and evaluation conditions were similar to that described above for the TWC systems that did not contain HC storage components.

RESULTS AND DISCUSSION

Improvements of the Al₂O₃/CeO₂/ZrO₂ Mixed Oxide

[Table 2](#) compares the specific surface area of the Al₂O₃/CeO₂/ZrO₂ mixed oxide and the (Al₂O₃ + CeO₂/ZrO₂) mixture after being calcined for 4 hours at 900, 1000, and 1100 °C, respectively. After the 900 °C calcination, the surface areas of the two materials are identical. A decrease in surface area is seen on both materials after the 1000 °C calcination. The Al₂O₃/CeO₂/ZrO₂ mixed oxide, however, maintains higher surface area compared to the (Al₂O₃ + CeO₂/ZrO₂) mixture, indicating that the Al₂O₃/CeO₂/ZrO₂ mixed oxide is thermally more stable.

Table 2. Specific surface area of the Al₂O₃/CeO₂/ZrO₂ mixed oxide and the (Al₂O₃ + CeO₂/ZrO₂) mixture after 900, 1000, and 1100 °C calcination

	Al ₂ O ₃ /CeO ₂ /ZrO ₂ mixed oxide	(Al ₂ O ₃ + CeO ₂ /ZrO ₂) mixture
900 °C/4hrs	127 m ² /g	127 m ² /g
1000 °C/4hrs	95 m ² /g	83 m ² /g
1100 °C/4hrs	56 m ² /g	57 m ² /g

The improved thermal stability of the Al₂O₃/CeO₂/ZrO₂ mixed oxide is further confirmed by the XRD analysis. The XRD patterns of the 1000 °C/4h calcined samples are shown in [Figure 1](#). Only a single CeO₂/ZrO₂ solid solution phase is observed with the Al₂O₃/CeO₂/ZrO₂ mixed oxide. In contrast,