Novel Concept Prototype of Low-Power-Consumption Electrically Heatable Catalyst

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Electrically heated catalyst devices (EHCs) are important for treating exhaust gases in the 20 to 120 s warmup period after a cold start when about 70% of the total hydrocarbon (HC) and carbon monoxide (CO) emissions from a modern gasoline powered vehicle are released. Although known for several years, EHCs have not been deployed because these devices are cost- and energy-intensive. An alternate EHC prototype proposed here is based on our reasoning that only the platinum group metals and the molecules undergoing oxidation need to be at light-off temperatures and it is not necessary to waste energy to heat the whole catalyst. The concept prototype, fabricated on a glass coupon, resistively heats the fluorine doped tin oxide film beneath the washcoat to bring a palladium-titania washcoat to the CO and HC light-off temperatures. The electrically powered concept prototype showed light-off temperatures of 250°C and 260°C for CO and HC, respectively, in laboratory tests with simulated exhaust gases at 25°C. A device based on this concept is estimated to attain the 1-kW target power consumption required for the deployment of the EHC.

Introduction

The emissions from modern gasoline vehicles are treated with a three-way catalyst (TWC) that simultaneously oxidizes HC and CO and reduces NO_x (Heck and Farrauto, 1995; Narula et al., 1996) at temperatures above 350°C. Currently, exhaust gas heat is the primary source of warming an automotive exhaust reduction catalyst. A catalyst typically requires a 20- to 120-s warmup period before it attains operational temperatures greater than 350°C from a cold start. During this warmup period, the catalyst is less efficient and untreated emissions are released into the environment (Figure 1). It has been shown that up to 70% of the total HC and CO tailpipe emissions, under a normal driving cycle, are released during this warmup period. Even though these catalyst systems meet current regulations, this emission of pollutants needs to be significantly reduced in order to meet the new goals of the ultralow emission vehicles (ULEV) program.

There are several technologies being currently evaluated to treat cold-start emissions on the basis of overall performance, cost, durability over the vehicle lifetime, packaging into the vehicle structure, and compatibility with existing vehicle components. They include electrically heatable catalysts (EHC) (Hurley et al., 1990), exhaust gas ignition (EGI) (Hurley et al., 1996), close coupled catalysts (Heck and Farrauto, 1995), and hydrocarbon trapping and its recycling (Pakko et al., 1994).

Electrically heated catalysts became available for testing in the late 1980s and have been shown to be very effective in reducing the emissions during warmup. The EHC devices rely on high-temperature resistance heaters to quickly warm the

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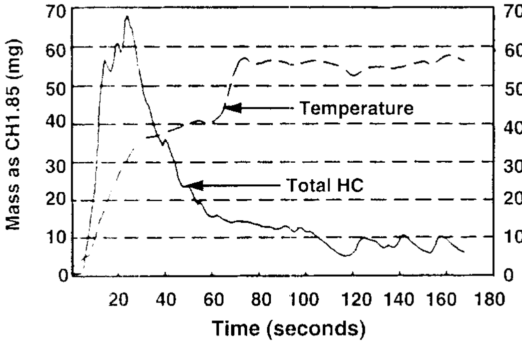

Figure 1. Total hydrocarbon emission from a vehicle as a function of time on a cold-start.

catalyst from cold start conditions (Whittenberger and Kubsh, 1991; Hurley et al., 1990; Heimrich et al., 1990). At first, the devices were power intensive and much of the development work focused on reducing the energy and power requirements. The approach generally involved reducing the mass of the electric resistive heater since a lower mass heater takes less energy to heat up. A consequence of reducing the mass of an EHC device is a reduction in the external surface area. Since high surface area is essential for the catalyst to be effective, several strategies have been investigated by the manufacturers of EHCs. However, the target electric power of 1 kW has not been attained with most full size commercial devices despite the advances made in EHC technology.

The most recently described EHC devices involve heating a substrate made of metal (Mizuno et al., 1994; Küper et al., 1994; Langen et al., 1994) and require 1.5–2.5 kW of power. The system, described by Küper et al., comes close to meeting the target electrical power requirements by combining a low mass EHC on a Porsche 968 with a catalyst positioned close to the engine and optimization of secondary air injection. However, the power requirements increase as the catalyst ages or if the catalyst is employed in automobiles with larger engines. A second design uses a screen-printed platinum layer on an alumina substrate to simultaneously heat the washcoat and catalyze the exhaust gas reactions (Häfele, 1994). This design meets the target power requirement but uses substantially larger amounts of very expensive platinum and requires additional improvements in overall durability to become feasible for long-term operation.

In our approach, we reasoned that since a typical catalyst becomes operational at about 350°C, the platinum group metals (PGMs) and the exhaust gas molecules need to be near 350°C to allow significant reactions during passage through the EHC. Since it is not feasible to heat the PGMs only, it is necessary to bring the PGM containing washcoat to light-off temperatures. Thus, there is no need to heat the entire catalyst monolith. Here, we present our findings that a conducting layer of doped tin oxide beneath the washcoat is adequate to heat the PGM containing washcoat of a three way catalyst in seconds after cold-start to initiate the catalytic oxidation of the HCs and CO (Narula et al., 1996). This reaction on the catalyst can in turn cascade an increase in temperature, due to chemical energy release, throughout the rest of the active catalyst. The fabrication of a concept prototype of an electrically heatable catalyst device and the test results on HC and CO oxidation are also presented.

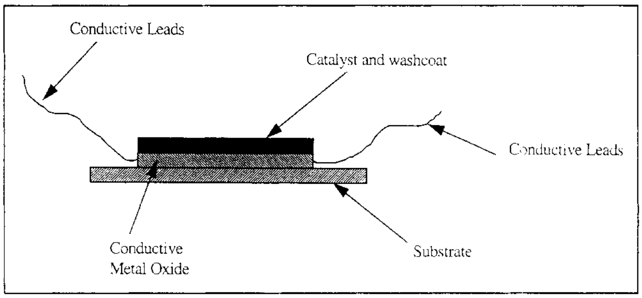

Figure 2. Electrically heatable catalyst concept prototype.

Experimental Studies

Fabrication of concept prototype

The concept prototype was fabricated from production low-e glass manufactured by the Libbey-Owens-Ford Company (Figure 2). The low-e glass is soda lime glass coated with a nonporous silica (SiO_2) barrier layer and a conductive film of fluorine doped tin oxide (SnO_2:F). Two gold leads were connected to the glass and the resistance was measured. This was followed by the deposition of a thin layer of titania (1,000 Å) employing sols prepared by treating titanium isopropoxide with acetylacetone, prior to hydrolysis. The thin film of titania was deposited on a 2 cm×2 cm glass coated with SnO_2:F using a Verax vertical dip coating apparatus which can produce a steady motion at a wide range of withdrawal rates. The rate of withdrawal was set at 0.4 cm/s. The film was fired at a rate of 2°C per min to 550°C and a hold time of 4 h. A 30 g/L solution of $PdCl_2$ was used to introduce Pd into the washcoat using a microsyringe. The $PdCl_2$ was decomposed by firing at 2°C per min to 550°C and a hold time of 4 h. The resistance of the device was measured again to ensure that the film deposition process did not adversely affect the fluorine doped tin oxide film on the substrate.

Test procedure

The concept prototype was placed in a flow reactor constructed from a 2-ft (0.6-m) section of 1-in. (25-mm) OD quartz tubing. The sample was heated in a programmable Lindberg TF55033A tube furnace or by the application of power from a Keithley 238 power supply. The temperature of the device was raised by ramping the current at a rate of 0.5 mA/s. The inlet gases (C_3H_6 and CO) were mixed in a manifold connected to a bank of computer operated mass-flow controllers. The test gases do not contain NO_x because there is very little NO_x present during cold start since the engine is fuel rich and operating below NO_x formation temperatures.

Gas samples from before and after the reactor flowed through standard gas analyzers to determine conversion efficiencies. Results are presented for CO and C_3H_6, which are normally used for testing automotive catalysts. The concentrations of CO and C_3H_6 in the flow reactor were set to 1 and 0.1%, respectively. The gas-flow rate was set at 100 sccm and a redox ratio (reductant/oxidant ratio) of 0.9. The conventional catalyst used for comparison of the conversion efficiencies was tested at $R = 0.5$. The conversion efficiency of the CO and hydrocarbons remains constant under lean conditions for $R < 1.0$. Thus, the test results at any value of $R <$

1.0 can be compared. These concentrations and flow rates simulate the total engine-out hydrocarbon level for modern vehicles which is typically ~800 to ~4,000 ppm C_1 (with 1 ppm C_3H_6 = 3 ppm C_1). A calculation of the ratio of diffusion to transport time for the concept prototype at 100 sccm in the test stand yielded a ratio of 0.3 compared to 0.35 in an operational automotive catalyst.

Results and Discussion

A concept prototype was fabricated in order to test the feasibility of heating only the washcoat, which incorporates the precious metal sites on a catalyst, to treat the exhaust gases during cold-start (Narula et al., 1996). The concept prototype was heated by the direct application of power to the fluorine-doped tin oxide conducting layer. The time required for the device to reach light-off temperatures was determined in a separate experiment, conducted outside the flow stand. The conductive layer was able to attain light-off temperatures instantaneously. The catalytic oxidation of CO and C_3H_6 as a function of temperature and power necessary to maintain that temperature is shown in Figure 3. The light-off temperature for CO occurs at ~250°C and requires ~4.1 W per 4 cm^2 area. C_3H_6 exhibits a light-off temperature of ~260°C and a power requirement of ~4.4 W per 4 cm^2 area. The light-off temperature is the temperature at 50% of maximum conversion and is often used as a normalized indicator of catalytic efficiency. These light-off temperatures compare favorably with experiments performed on an equivalent substrate loaded with a conventional automotive catalyst and tested in the same flow reactor (Figure 4). The conversion efficiency is dependent on the reactor and test prototype configuration as well as the gas-flow rate and choice of platinum group metal. The results for CO and C_3H_6 are qualitatively similar. At low temperatures, the reaction is limited by kinetics and the curves exhibit an Arrhenius type behavior. At high temperatures, however, mass transfer becomes the limiting factor, the curves flatten out, and conversion increases only slowly with temperature. In this regime, more CO is converted than C_3H_6. This can be explained by the difference in the diffusive behavior of the reactants.

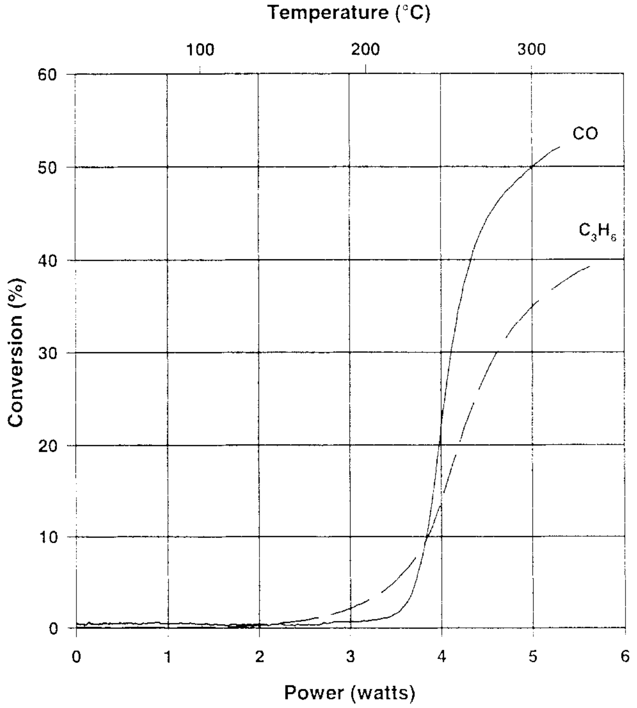

Figure 3. Light-off performance as a function of electrical power and temperature for an electrically heatable catalyst prototype operating at R = 0.9 (ratio of reductant/oxidant), and gas concentrations of 1% CO and 1,000 ppm C_3H_6.

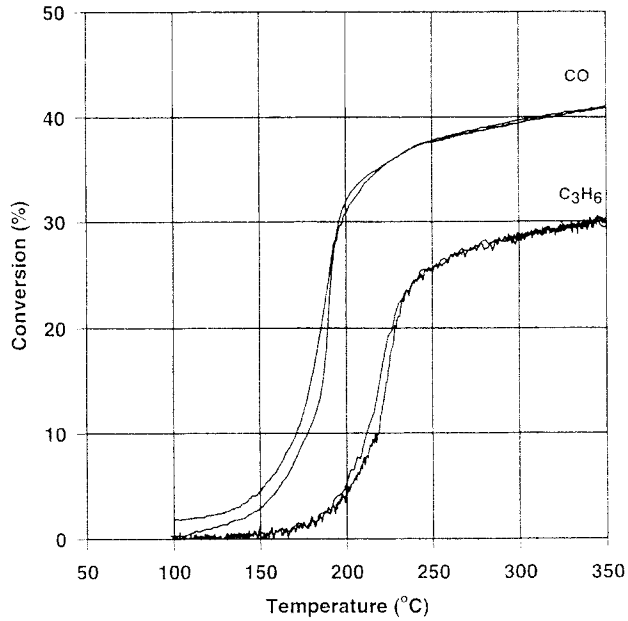

Figure 4. Light-off performance of a commercial automotive catalyst operating at R = 0.5 (ratio of reductant/oxidant), and gas concentrations of 1% CO and 1,000 ppm C_3H_6.

The preliminary data for this prototype represent the power required to heat the PGM containing washcoat to the light-off temperatures, as well as to compensate for the heat convected away from the surface by room temperature gas reactants. This temperature gradient present at the start of the experiment remains constant throughout the experiment. This is in contrast to an EHC on a vehicle, where the exhaust also contributes towards warming the catalyst. This reduces the convective demand on power.

Our power estimates, based on space velocities comparable to conventional catalysts, suggest that an EHC device with a 1 kW or less power requirement is possible based on 4.1 W per 4 cm^2, and a heat exchange area of approximately 500–1,000 cm^2. This power estimate does not include the reduced convective demand or any improvements in power consumption that can be harnessed by any cascaded temperature increases on the catalyst due to chemical energy release.

Feasibility

The economical fabrication of an on-board testing EHC device based on our concept prototype is feasible for the most part from existing technology. The deposition of conductive thin films with their associated electrical leads on a honeycomb substrate is difficult. A more feasible design might utilize stacks of alternating sheets of corrugated and flat alumina to form a substrate. Conducting films can be either metal, metal nitrides/carbides, or metal oxides. However, metal and metal nitride/carbide films would be relatively expensive to deposit because of the cost of physical deposition methods. Among the oxide based conducting materials, doped tin oxides and zinc oxides are viable candidates provided they can be deposited by solution methods such as the sol-gel process.

We have previously demonstrated the deposition of a washcoat from sol-gel processed alumina on a cordierite honeycomb (Narula et al., 1993). This process can be employed to deposit washcoats on a variety of substrate configurations.

Conclusions

In conclusion, we have shown that heating the PGM containing washcoat is adequate to treat automotive exhaust gases after cold-start. The simplicity of the concept prototype can be easily translated into an on-board test EHC from commercially available technologies.

Acknowledgment

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