Abstract
Regulations that limit emissions of pollutants from gasoline-powered cars and trucks continue to tighten. More than 75% of emissions through an FTP-75 regulatory test are released in the first few seconds after cold-start. A factor that controls the time to catalytic light-off is the heat capacity of the catalytic converter substrate. Historically, substrates with thinner walls and lower heat capacity have been developed to improve cold-start performance. Another approach is to increase porosity of the substrate. A new material and process technology has been developed to significantly raise the porosity of thin wall substrates (2-3 mil) from 27-35% to 55% while maintaining strength. The heat capacity of the material is 30-38% lower than existing substrates. The reduction in substrate heat capacity enables faster thermal response and lower tailpipe emissions. The reliance on costly precious metals in the washcoat is demonstrated to be lessened. The microstructure of the new substrate material is optimized for washcoat compatibility and to maintain strength. The new materials are confirmed to be thermomechanically robust for service in the harsh exhaust system environment.

Introduction
Societal concerns about the environment, human health, and quality of life are driving enactment of tighter regulations of emissions of greenhouse gases and pollutants like hydrocarbons and NOx from passenger cars. In 2012, the US Environmental Protection Agency (EPA) and Department of Transportation (DoT) established targets for fleet average fuel economy to help control emission of carbon dioxide and slow global climate change [1]. Most recently, the US EPA set forth the Tier 3 standard that mandates reductions in combined nonmethane organics (NMOG) and NOx from 86 to 30 mg/mi [2]. On full implementation, vehicles sold into the United States in 2025 will have roughly double the fuel economy and emit one half as much carbon dioxide as those manufactured in 2010. A similar body of regulations is being phased in within the European Union [3]. The Euro6 standard when fully implemented in 2020 calls for a reduction in carbon dioxide emissions from 135 to 95 g/km. The regulations include provisions to address engine operating conditions outside of the certification cycle. Passenger cars will be required to comply with NOx, HC, CO and soot number limits when tested using a drive cycle that more accurately reflects real-world conditions.

More than 75% of emissions of CO, NOx and HC from gasoline-powered vehicles equipped with close-coupled catalytic converters are released in the first few seconds after cold-start [4]. Times to catalytic light-off are shortened by reducing the volumetric heat capacity of the substrate [5]. Once heated, catalytic conversion is strongly affected by kinetics of mass transfer. Substrates with thinner walls and higher cell density improve cold-start and hot-drive conversion of pollutants [5, 6]. Wall thickness has been decreased progressively from 165 to less than 75 μm [6]. The lower heat capacity of thin wall substrates speeds catalyst light-off. Thinner walls also enable a reduction in pressure drop and make more space available to hold washcoat.

Further improvement of cellular ceramic catalyst supports can facilitate compliance with the new and tighter emissions regulations, lessen reliance on costly precious metal catalysts, and enable compact system design. Another approach to improve cold-start performance described in the patent literature is to increase the porosity of the substrate [7, 8]. The challenge with this approach is to maintain strength for handling and survival within the rough environment of the aftertreatment system. Strength of ceramic materials decreases exponentially with porosity [9]. Porosity of commercially available thin-wall cordierite substrates is typically between 27 and 35% [10]. In this paper, we describe development and validation of a new cordierite substrate material that has a porosity of 55%. The heat capacity is lowered by 30-38% over existing commercially available cellular ceramics of the same cell density and wall thickness. Faster
thermal response and earlier catalytic light-off are demonstrated in laboratory and on-vehicle tests that compare standard to high porosity substrates for 600/3 and 600/2 cellular designs. Note, the first number in terms like 600/3 and 600/2 is cell density in units of cells/in², and the second number is the thickness of the wall in units of 10⁻³ in obtained after rounding down to the nearest integer value. Besides the additional porosity, the microstructure of the new material is engineered for washcoat compatibility, washcoat utilization, strength for handling, and thermomechanical durability. The properties and microstructures of the new, high porosity FLORA™ substrates are compared to Celcor® substrates with standard porosity in Table 1 and Figure 1, respectively.

Table 1. Comparison of properties that are typical for standard and high porosity 600/3 and 600/2 substrates. Porosity and mean pore diameter were determined by mercury porosimetry, and elastic modulus was characterized by the sonic resonance technique [11].

<table>
<thead>
<tr>
<th>Property</th>
<th>Standard Porosity</th>
<th>High Porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>600/3</td>
<td>600/2</td>
</tr>
<tr>
<td>Porosity (%)</td>
<td>33</td>
<td>27</td>
</tr>
<tr>
<td>Mean pore diameter (µm)</td>
<td>4</td>
<td>1.3</td>
</tr>
<tr>
<td>Thermal expansion coefficient (×10⁻⁷°C)</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>Modulus of rupture (MPa)</td>
<td>2.01</td>
<td>1.39</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>4.49</td>
<td>3.63</td>
</tr>
<tr>
<td>Density of matrix (g/L)</td>
<td>294</td>
<td>248</td>
</tr>
</tbody>
</table>

Figure 1. SEM micrograph comparing microstructures of (a) high and (b) standard porosity substrates with 600/3 designs.

**Laboratory Bench Reactor**

A specialized laboratory bench reactor was built to characterize catalytic function and the impact of the substrate on catalytic conversion including light-off phenomena. A schematic of the reactor flow column is shown in Figure 2. Inert gases and steam that constitute more than 98% of the simulated exhaust gas are fed through a resistive heating element. Reactive gases like carbon monoxide and hydrogen are injected immediately downstream of the heater. Temperature of the reactive gas at the entrance to the sample is under closed-loop control through modulation of power to the heating element. After passing through the sample, gases are analyzed by an MKS 2030 HS FTIR. The flow column was constructed from thin-gauge stainless steel so that rapid temperature transients may be delivered to the sample. Heating rates of up to about 1000°C/min, similar to the face of a close-coupled converter, are possible. The high speed FTIR characterizes changes in conversion at a rate of 5 Hz. Steady-state conversion and time to light-off were characterized with a gas formulation of 0.5% CO, 0.05% NO, 0.04% C₂H₆, 0.11% H₂, 0.54% O₂, 13.1% CO₂, 10% H₂O, and the remainder N₂; thermal response speed was determined with N₂ so that there is no heat released due to oxidative reactions on the catalyst that could change the sample temperature. Unless otherwise noted, samples used in these tests measured 50 mm in diameter and 25.4 mm long.

![Figure 2. Schematic of the laboratory bench reactor.](Image)

**Thermal Response and Light-off**

**Analysis**

The first step in reaching catalytic light-off is for catalysts in the converter to warm to a temperature where they are active. The process of heat transfer has been analyzed to identify the key parameters that control the time to heat the converter. The fluxes of heat into and out of the converter are

\[
\dot{q}_{in} = \nu A C_g T_i
\]

and

\[
\dot{q}_{out} = \nu A C_g T_o
\]

respectively, where “ν” is the linear velocity of gas flowing into the converter, “A” is the cross-sectional area of the converter, “C_g” is the heat capacity of the gas, and “T_i” and “T_o” are the temperature of the gas at the inlet and outlet, respectively. The exchange of heat that takes place between the gas and converter is proportionate to the internal surface area, “S”, a coefficient for rate of heat transfer between the converter and the gas within its channels, “h”, and the temperature difference between the gas and the converter, “T_g - T_c”

\[
\dot{q}_{g-c} = h S (T_g - T_c)
\]

The rate of change of temperature of the exhaust gas and converter are obtained from the difference in heat entering and leaving the system

\[
\frac{dT}{dt} = \frac{1}{m} \left( \dot{q}_{in} - \dot{q}_{out} - \dot{q}_{g-c} \right)
\]
respectively, where “\(l\)”, “\(x_g\)”, and “\(C_c\)” are the length, open frontal area, and heat capacity of the converter, respectively. The open frontal area is defined as the ratio of the cross-sectional areas of a channel to the repeating cell unit. A governing differential equation that describes temperature of the converter as a function of the inlet temperature is obtained by substitution of equations (1), (2), and (3) into equations (4) and (5) under the condition that \(T_g = T_o\)

\[
\frac{d^2 T_c}{\dot{v} r h} \frac{d^2 T_c}{dt^2} + \left( \frac{C_c}{\dot{v} x_g C_g} + \frac{C_c}{r h} + \frac{1}{\dot{v}} \right) \frac{dT_c}{dt} + T_c = T_i
\]

Note that the following respective substitutions for space velocity and surface-to-volume ratio were made in writing equation (6)

\[
\dot{v} = \frac{v}{lx_g}
\]

and

\[
r = \frac{S}{l A}
\]

**Time Constants of the System**

Each combination of coefficients that precedes derivatives of \(T_c\) with respect to time in equation (6) is a time constant for the system. A rapid temperature response of the converter for fast light-off occurs when these time constants are made as small as possible. The heat capacity of the converter appears in three out of four of the constants. Reducing the heat capacity of the converter either through design or by changes in the nature of the substrate or washcoat materials will speed the thermal response. The heat capacity of the converter with the contribution of the substrate, \(C_s\), expanded to make the impact of design and materials evident is

\[
C_c = w \sqrt{c} (2 - w \sqrt{c}) (1 - p) C_{p\text{Cordierite}} + C_w
\]

where “\(c\)” is the cell density, “\(w\)” is the substrate wall thickness, “\(p\)” is the fraction of pores in the substrate, “\(C_{p\text{Cordierite}}\)” is the intrinsic heat capacity of cordierite, and “\(C_w\)” is the heat capacity of the washcoat. For fast light-off, substrates with thin walls, low cell density, and high porosity are preferred. The washcoat presents an interesting situation. It is necessary for conversion of pollutants. At the same time, it increases heat capacity thereby degrading light-off performance. The amount of washcoat must be tuned for light-off and steady-state performance.

The relative contributions of each time constant to the system have been examined. A few cases are provided in Table 2 for a washcoat load of 200 g/L on standard and high porosity substrates in several designs. The values in the table show that for a range of materials, designs, and washcoat loads, the dominant time constant for heating of a catalytic converter is \(b_1\). Although \(b_1\) may be influenced somewhat by the open frontal area, it is primarily controlled by the heat capacity of the converter. The next largest time constant in the system is \(b_2\). It is proportionate to the heat capacity of the converter, as well, but it can also be affected by the design of the converter through the surface to volume ratio. For the conditions listed in the table, it is roughly 20% of \(b_1\), so its contribution to thermal response speed is modest and primarily through the heat capacity of the converter. The time constants \(a\) and \(b_1\) are negligible in comparison to \(b_1\) and \(b_2\) and will be dropped from further discussion as they do not contribute appreciably to warm-up performance. Heat capacity is the primary factor controlling thermal response speed of the converter, and the time rate of change of temperature of the converter given by equation (6) simplifies to

\[
b \frac{dT_c}{dt} + T_c = T_i
\]

Where

\[
b = C_c \left( \frac{1}{\dot{v} x_g C_g} + \frac{1}{r h} \right)
\]

**Table 2. Comparison of system time constants for thermal response speed for selected standard and high porosity substrate designs. In the calculations, the washcoat has a heat capacity of 1 J/g/cm^3 and density of 2.18 g/cm^3, the temperature is 300°C, and space velocity is 150 k/hr.**

<table>
<thead>
<tr>
<th>Time constant (s)</th>
<th>Standard Porosity</th>
<th>High Porosity (55%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a = \left( \frac{C_c}{\dot{v} r h} \right)^{1/2} )</td>
<td>0.4</td>
<td>0.4</td>
</tr>
<tr>
<td>(b_1 = \frac{C_c}{\dot{v} x_g C_g} )</td>
<td>28.0</td>
<td>24.3</td>
</tr>
<tr>
<td>(b_2 = \frac{C_c}{r h} )</td>
<td>6.3</td>
<td>5.6</td>
</tr>
<tr>
<td>(b_3 = \frac{1}{\dot{v}} )</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>(C_s (J/cm^3/°C) )</td>
<td>0.52</td>
<td>0.48</td>
</tr>
<tr>
<td>(x_g )</td>
<td>0.73</td>
<td>0.77</td>
</tr>
<tr>
<td>(r (1/m) )</td>
<td>3300</td>
<td>4100</td>
</tr>
</tbody>
</table>

The impact of porosity of the substrate on thermal response speed of the converter can be seen in the time constants presented in Table 2. For the case of a 600/2 design, the high porosity substrate has a 38% lower heat capacity than the standard porosity substrate. Addition of 0.2 g/cm^3 of washcoat raises the heat capacity of converters based upon each substrate by 0.2 J/cm^3. The added washcoat reduces the
difference in heat capacities that will influence light-off performance. The converter with the high porosity substrate has a ∼22% lower heat capacity than one utilizing standard porosity material. The difference in sums of system time constants is somewhat larger; the converter with the high porosity substrate should be 28% faster in thermal response.

**Thermal Response**

Catalytic converters that use high porosity substrates have thermal response speed that is faster than honeycomb substrates made with standard porosity materials. The thermal response speed, “b” from equation (10), was measured for standard and high porosity materials in several designs with a commercial three-way catalyst washcoat at a loading of 275 g/L. Experimental determination of “b” was made by ramping the temperature of gas flowing into the inlet from 110 to 450°C at a rate of 700°C/min. The space velocity was 60,000 hr⁻¹.

The temperature at the outlet of the converter was monitored. Solution of equation (10) for a linear temperature ramp a rate of “η” at the inlet is

\[ T_i(b,t) = \eta t - b(1 - e^{-\frac{t}{b}}) + T_i(0) \]  

For times after initiation of the ramp such that \( t \gg b \), the temperature at the outlet increases at the same rate as the inlet but with a delay. Taking the limit of equation (12) for \( t \gg b \) shows that the delay is the thermal response speed

\[ T_o(b,t) = \eta(t - b) + T_i(0) \]  

The faster thermal response speed of the high porosity material is illustrated in Figure 3. Temperature at the inlets in both cases is nearly identical. The outlet temperature of the high porosity sample reaches any given temperature during the thermal ramp earlier than the sample with standard porosity. After an initial transient, the temperature at the outlet increases at a rate similar to the outlet but with a delay as expected according to equation (13).

![Figure 3](image4.png)

The thermal response speed, \( b \), is defined for experimental purposes as the difference in times for the inlet and outlet locations to reach 250°C. The high porosity 600/2 converter sample responds 21% faster than the reference.

Thermal response speeds of standard and high porosity materials are plotted for several designs in Figure 4. Density of the converter samples is used as a surrogate for heat capacity. This is possible because the washcoat concentration is fixed at 275 g/L; its contribution to the total heat capacity is the same across the cases presented in the plot. However, the contribution of the substrate depends upon its density which changes with cell density, wall thickness, and porosity. For these reasons, thermal response speed correlates strongly with density of the converter samples. The high porosity substrate materials have faster thermal response speeds due to the heightened porosity.

![Figure 4](image5.png)

**Catalytic Light-off**

The faster thermal response associated with the lower heat capacity of the high porosity substrates leads to earlier catalytic light-off and reduced reliance on precious metals to convert emissions that are released during cold-start. This was demonstrated in laboratory bench reactor studies for high and standard porosity substrates in the 600/2 design. Substrates of each material type were commercially washcoated with 275 g/L of three-way catalyst at two precious metals concentrations, 40 and 100 g/ft³. Samples were aged at 950°C for 24 hr in 10% \( \text{H}_2\text{O} \). Thermal response speed and time to light-off were determined at space velocities of 30,000 and 60,000 hr⁻¹. Light-off conversion traces for the 100 g/ft³ concentration of precious metal catalyst are compared for propene in Figure 5. There is earlier conversion on the converter sample that uses the high porosity substrate. The time to reach 50% conversion of propene is more than two seconds faster with the high porosity sample. Once the catalysts are heating, conversion in both samples becomes roughly equivalent, ∼97%. The same features are observed for carbon monoxide conversion on the high and standard porosity substrates.

![Figure 5](image6.png)
The time to light-off as defined by 50% conversion for propene correlates with thermal response speed as shown in Figure 6. At a given space velocity and precious metal catalyst concentration, the lower weight, lower heat capacity, high porosity substrate has superior light-off performance.

The enhanced light-off performance of the high porosity substrate material lessens the amount of precious metal catalyst required to meet an emissions reduction target. Examination of Figure 6 shows that times to light-off partition into two groups based upon the concentration of precious metals. Regression analysis of data from each set of precious metals concentration shows that there is a strong correlation between time to light-off and thermal response speed. The analysis makes clear that light-off occurs earlier in samples with the high precious metals concentration. It also shows that the time to light-off is more sensitive to thermal response speed at the lower, 40 g/ft³ precious metal catalyst concentration. The amount of precious metal reduction possible with use of a lower heat capacity substrate can be estimated from the correlation of time to light-off with thermal response speed. In Figure 6, similar times to 50% conversion of propene are observed with the high porosity material at a precious metal concentration of 40 g/ft³ and standard porosity material at 100 g/ft³. This corresponds to more than a 1 g reduction in precious metals required in a typical 1 L converter.

**On-Vehicle Emissions Testing**

Demonstration of the light-off benefits of high porosity substrates was made on a SULEV-compliant vehicle with a 2.4 L engine that has a rated power of 158 hp at 6,000 rpm. The high and standard porosity substrates in the 600/2 design were prepared in the same size as the close-coupled converter originally installed on the vehicle, 105.7 mm in diameter by 105 mm long. The substrates were commercially coated with 275 g/L of three-way catalyst with a precious metal concentration of 40 g/ft³. The converters were aged at 950°C for 24 hr in 10% H₂O in a laboratory oven prior to canning to simulate use.

Emissions tests were conducted at a facility designed for measurement of the low emission levels of a SULEV vehicle. The vehicle was conditioned after installation of each type of converter by driving on a 1.3 m Horiba chassis dynamometer through FTP-75, US06, and LA4 cycles. Emissions during FTP-75 tests were measured in real-time before and after the close-coupled converter with Horiba MEXA-7000 series sampling and analysis equipment including low emissions analyzers. Two FTP-75 tests were conducted for each converter on subsequent days with overnight cold soaks. Temperatures at the inlet near the center of the face and 12.5 and 37.5 mm into the bed were monitored as were engine control parameters. Faster thermal response and improved light-off performance observed in laboratory tests with high porosity substrates were confirmed. As shown in Figure 7, the temperature 12.5 mm deep in the converter with the high porosity substrate was 100°C hotter than the converter with a standard porosity substrate. It takes an additional 2.5 s for the standard porosity converter to reach the same temperature. The temperature responses at 37.5 mm depth show the same trend; the converter with the high porosity substrate heats more rapidly. The faster warm up of the converter with the high porosity substrate reduces cold-start emissions as shown by Figure 8.
Hydrocarbon emissions 30 s after vehicle start after the close-coupled converter are 24% lower for the high porosity substrate than with the standard porosity substrate.

**Optimization of the High Porosity Substrate**

An increase in porosity of a catalytic converter substrate lowers its heat capacity for faster thermal response and earlier light-off. It also affects other aspects of substrate performance. The challenge in developing a high porosity, thin-walled catalytic converter substrate has been to ensure that all product requirements are satisfied and that methods to create porosity are suitable for manufacturing. There are many ways that the increased porosity influences product performance. Some of the most significant are strength required for handling and canning, interactions with the washcoat process, and thermal shock performance.

**Strength**

Pore microstructure affects strength of brittle ceramic materials in two ways. At higher porosity, there is less material available to support loads so strength will be lower than for a comparable material that has lower porosity. Studies with brittle ceramic materials like cordierite show strength drops exponentially as porosity increases [12, 13]. The size of pores also affects strength. Higher strengths are realized in the same material for smaller pore size [14, 15]. These same findings apply to cordierite.

Figure 9 shows the four-point modulus of rupture of cordierite materials. Testing was performed with support and load spans of 101.6 and 50.8 mm, respectively, on samples that are nominally 25.4 mm wide by 12.5 mm thick with channels parallel to the long axis of the sample. The modulus of rupture of reference cordierite material that is the basis for standard porosity substrates drops rapidly as porosity increases. At 55% porosity, the modulus of rupture is more than a factor of two lower than the standard substrate material which has a porosity of 35%. The pore microstructure of the high porosity material was refined for strength at higher porosity. Raw materials including those required to form porosity were selected to reduce the proportion of pores that are large in size that can degrade strength. Both materials have similar porosity, 55%, and mean pore sizes, ~4 μm. However, the new, high porosity material has many fewer pores that are large in size, >8 μm. The new, high porosity material is more than 60% stronger by this measure than reference cordierite at the same porosity.

The new, high porosity material has strength to withstand external compressive forces required for canning and in-use catalyst retention. Strength for canning was characterized by an isostatic test. Standard and high porosity substrates were sealed in a fitted rubber container. The rubber container was immersed in a water-based hydraulic fluid. The isostatic pressure in the fluid was increased until the substrate failed. As shown in Figure 10, the isostatic strength of the high porosity material is above 10 bar and similar to standard porosity 600/2.

**Catalytic Activity and Steady-State Mass Transfer**

The microstructure of a high porosity cellular ceramic influences access of pollutants to catalyst sites. Depending upon porosity and pore size, a washcoat may deposit nearly exclusively onto the surface of the walls or fill up most of the pores. Washcoat that is in the pores
does not occupy space in the channels so lower pressure drop may be
realized. However, pollutants must diffuse through a smaller cross
section and over longer distances to react within catalyst sites within
the washcoat that is in the wall [16]. The high porosity substrate may
have superior light-off performance due to a reduction in heat
capacity, but once heated, catalytic conversion is impaired due to
slower mass transfer. The microstructure of the substrate may be
engineered to either allow or inhibit penetration of washcoat particles
into the wall. A recent example is use of porous substrate walls to
host zeolite washcoat for selective catalytic reduction (SCR) to lower
pressure drop and simultaneously increase the catalyst load [17].

The impact of microstructure on penetration of washcoat into the
substrate wall and on activity of three-way catalyst was studied as part
of the material design process. Substrates with cell densities of 93
\( \text{cm}^{-2} \) (600 in\(^2\)), and wall thickness of \( \sim \)95 \( \mu \text{m} \) were prepared with
porosities of 46 and 67% and mean pore diameters of 3 and 8 \( \mu \text{m} \),
respectively. The 50 mm diameter substrates were coated with a 0.2 g/
\( \text{cm}^3 \) of a model three-way washcoat. The base formulation consisted
of 60% by weight La-stabilized 13-alumina and 40% ceria/zirconia
loaded with 200 g/ft\(^3\) of precious metal catalyst with a Pt:Pd:Rh ratio
of 1:10:1. The washcoat slurry was applied by vacuum pull method.
The coated substrates were dried and fired at 700°C for 5 hr.

SEM analysis showed deep penetration of the three-way washcoat
into the walls of the substrate with 67% porosity (Figure 11). The
washcoat did not penetrate into the wall of the substrate with the
lower porosity and smaller mean pore diameter. The composite
microstructure impacted catalytic function in the laboratory bench
reactor studies. A slow ramp, 0.5°C/s, was utilized to produce near
steady-state conditions between temperatures of 110 and 450°C.
Catalytic conversion of carbon monoxide is compared for the two
substrate types in Figure 12. The efficiency of conversion with the
67% porosity substrates is noticeably lower than for the substrate
with 46% porosity. The reduced conversion is consistent with a mass
transfer limitation.

![Figure 11. SEM micrographs of substrates with (a) 46% porosity and 3 \( \mu \text{m} \)
mean pore diameter and (b) 67% porosity and 8 \( \mu \text{m} \) mean pore diameter after
application of 0.2 g/cm\(^3\) of three-way catalyst washcoat.](image)

![Figure 12. Carbon monoxide conversion for substrates with (a) 46% porosity
and (b) 67% porosity washed coated with 0.2 g/cm\(^3\) of three-way catalyst.](image)

A high porosity substrate microstructure that aids in deposition of
washcoat onto the wall is preferred for efficient use of costly catalyst
materials and to meet stringent emissions regulation. Studies of the
interaction of high porosity substrates with three-way washcoat show
that it deposits primarily onto the wall. The median size of particles
in the model three-way washcoat was varied between 2 and 5 \( \mu \text{m} \) by
ball milling. For this range of washcoat particle sizes, there was no
detectable penetration of washcoat into the walls of the high porosity
substrate as illustrated in Figure 13. Even for the 2 \( \mu \text{m} \) washcoat
particle size, the washcoat is entirely localized to the wall surface.
The same behavior, washcoat deposition on the wall, has been
observed with commercially applied three-way catalyst washcoats.

The steady-state catalytic conversion efficiency with high porosity
substrates is similar to substrates with standard porosity. Substrates of
each material were commercially coated with 275 g/L of three-way
catalyst. The precious metals concentration was 100 g/ft\(^3\). Cores for
laboratory bench reactor tests were aged at 950°C for 24 hr in 10%
H\(_2\)O. Conversion traces for CO and propene are presented in Figure
14. Conversion on the high porosity samples with washcoat on the
wall is similar to samples with standard porosity.

![Figure 13. SEM micrographs of polished cross-sections of high porosity
(55%) substrates average particle sizes of (a) 2 \( \mu \text{m} \) and (b) 5 \( \mu \text{m} \) after
washcoating with three-way catalyst.](image)
Figure 14. Steady-state conversion of CO and C3H6 for commercially catalyzed 600/2 standard and high porosity substrates. The washcoat load is 275 g/L and has a precious metals concentration of 100 g/ft³.

**Thermomechanical Durability**

Catalytic converter substrates provide a mechanical support to hold washcoat. The composite material must withstand the large and rapid temperature changes that occur within an exhaust system. Although the properties of the substrate serve as a foundation for the mechanical behavior of the system, it is the composite properties that determine survivability. Survival tests were performed on standard and high porosity 600/3 substrates that measured 105.7 mm diameter by 114.3 mm in length. The substrates were commercially washcoated with three-way catalyst. The coated properties are listed in Table 3. Elastic modulus was determined by the sonic resonance method described in ASTM 1198-01 for samples that are nominally 150×50×25 mm in size [11] with channels oriented parallel to the long axis.

Rapid temperature transients to induce thermal stresses in the standard and high porosity 600/3 substrates were generated with a 35 kW natural gas powered Kromschröder burner. The ability of a substrate to withstand repetitive heating and cooling cycles similar to what would be experienced in an exhaust system, its survivability, was assessed with the following protocol. Coated substrates were cycled 5 times between 100 and 650°C with 30 s to reach the setpoint, 90 s to hold, and 90 s to cool. After each set of 5 cycles, the sample was inspected for cracks visually and by contact ultrasound working with an EPOCH 4 flaw detector and Videoscan transducer, both manufactured by Panametrics-NDT™. The ultrasound inspection method is described in U.S. Patent 7,614,304 [18]. If no cracks were detected, the sample was subjected to an additional 5 cycles to a set-point that was raised by 25°C. The procedure continued until a crack was detected. The inlet temperature profile for a 900°C set point is shown in Figure 15. The rapid change in temperature at the inlet creates a temperature differential along the length of the sample. The temperature differential becomes progressively larger as the set-point temperature is raised. Failure temperatures for standard and high porosity substrates are shown in Figure 16; they are statistically the same. These results show that the high porosity 600/3 substrates have in-service durability that is similar to 600/3 substrates with standard porosity.

Table 3. Comparison of coated physical properties for standard and high porosity 600/3 substrates with a 250 g/L commercial washcoat.

<table>
<thead>
<tr>
<th>Property</th>
<th>Standard Porosity 600/3</th>
<th>High Porosity 600/3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal expansion coefficient (10⁻⁶/°C)</td>
<td>8</td>
<td>6</td>
</tr>
<tr>
<td>Axial modulus of rupture (MPa)</td>
<td>2.9</td>
<td>1.7</td>
</tr>
<tr>
<td>Axial elastic modulus (GPa)</td>
<td>6.5</td>
<td>3.3</td>
</tr>
</tbody>
</table>

Figure 15. Burner temperature profile for survivability testing at 900°C

Figure 16. Temperatures of failure in survivability tests for washcoated standard and high porosity 600/3 substrates. Error bars are standard deviations for three samples.

**Summary**

New, high porosity substrates with 30-38% lower heat capacity than standard substrates were demonstrated to reduce cold-start emissions from gasoline-powered vehicles by 24%. The new substrates will aid in compliance with tighter emissions regulations. The microstructure of the new substrate material was optimized for strength, washcoat compatibility, catalytic performance, and thermomechanical durability. The superior light-off performance expands the design space. Laboratory bench reactor studies show the new substrates can reduce the amount of precious metals to achieve an emissions objective. A lower cell density substrate design working with the high porosity material can achieve the same emissions as a traditional substrate while delivering a lower pressure drop. More compact system designs are also possible. In each of these cases, optimization
of the substrate, washcoat, and system design are required. Application performance attributes of high porosity substrates are described in more detail in a separate SAE paper.

References


