Developments in Advanced Ceramics and Composites

A collection of papers presented at the 29th International Conference on Advanced Ceramics and Composites, January 23-28, 2005, Cocoa Beach, Florida

Editors
Manuel E. Brito
Peter Filip
Charles Lewinsohn
Ali Sayir
Mark Opekà
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General Editors
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The 29th International Conference on Advanced Ceramics & Composites was held in Cocoa Beach Florida, January 24-28, 2005. This unique proceedings contains papers from scientists and engineers in government, industry, and academic organizations from around the world which were presented in the following symposia and focused sessions:

- Ceramics in Environmental Applications
- Multifunctional Material Systems Based on Ceramics
- Carbon/Carbon and Ceramic Composite Materials in Friction
- Reliability of Ceramic and Composite Components
- Characterization Tools for Materials Under Extreme Environments
- Functional Nanomaterial Systems Based on Ceramics

We would like to thank and express appreciation to those who attended and participated in the meeting, to the session chairs and organizers, and to those who helped us in the review of the manuscripts contained in this volume.

Manuel Brito
Peter Filip
Charles Lewinsohn
Ali Sayir
Mark Opekka
William Mullins
Ceramics in Environmental Applications
CHARACTERIZATION OF MnO-DOPED LANTHANUM HEXALUMINATE (LaMnAl\(_{10.19}\)) IN TERMS OF SELECTIVE CATALYTIC REDUCTION OF NO\(_x\) BY ADDITION OF HYDROCARBON REDUCTANT (HC-SCR)

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ABSTRACT

Environmental pollution by vehicles, turbines and aircrafts has enormously increased in the last decade. New generation lean-burn combustion engines which are more effective and require less fuel consumption will raise the emission of nitrogen oxides (NO\(_x\)) even more. Thus, especially in urban areas, more stringent environmental regulations are to release which can only be met by development of new catalytic materials and concepts.

Rare earth oxide catalysts are reported to offer highly effective conversion of NO\(_x\) by methane (CH\(_4\)) in the terms of selective catalytic reduction (HC-SCR). Especially La\(_2\)O\(_3\) is reported to have a high NO reduction by CH\(_4\) to N\(_2\), although its technical realization as catalyst material has not yet reported and can be challenging due to the hydroscopic property of La\(_2\)O\(_3\).

Complex oxide compounds containing La\(_2\)O\(_3\) however can be suitable alternatives and promising candidates for technical application as catalysts. In this study, LaMnAl\(_{10.19}\) is characterized in terms of HC-SCR with methane. Phase and morphological characterization of the powder synthesized by sol-gel route and coatings by electron-beam physical vapor deposition (EB-PVD) deposition was presented. LaMnAl\(_{10.19}\) crystallizes to the magnetoplumbite phase at about 1000°C and is then thermally stable up to 1400°C.

FTIR spectra of pressed sol-gel powder showed that NO is adsorbed superficially and oxidized by the surface. The addition of oxygen led to changes of the spectrum in the nitrite-nitrate region and the formation of NO\(^+\) and N\(_2\)O\(_4\) species. The EB-PVD coated LaMnAl\(_{10.19}\) layer was catalytically characterized at 200\(^\circ\), 400\(^\circ\) and 600 \(^\circ\)C and showed catalytic activity towards NO depending on temperature.

INTRODUCTION

In the last decade, the need for low fuel consumption and high efficiency turbines and motors has promoted the use of lean-burn techniques leading to an increase in the combustion temperature. The consequent increase of cyclic process parameters raises the emission of NO\(_x\) and leads to formation of oxygen rich exhaust gases. On the other hand, more stringent regulations have been released by legislators such as CEAP, LAER or EURO regarding emissions. As an intermediate precaution, NO\(_x\) and hydrocarbon (HC) emissions are reduced to 0.3 g/km for diesel engines and almost to zero for petrol engines with the EURO4 regulation which is to apply from 2005. Further adjustment of the diesel and petrol engine regulations has been discussed for the future regulations \(^1\). From 2008, with the new CEAP6 regulation for aircraft turbines, NO\(_x\) emissions are to reduce to a level far below the former CEAP2 regulation \(^2\).

It is to expect that total emission further increases with the increase of the worldwide air traffic. European commission aims to achieve efficient and environment-friendly energy generation by targeting low to zero emission in power plant technologies and aircraft traffic.

Referring to these considerations more stringent regulations are anticipated in the future, particularly, for turbine engines operated in urban areas, emphasizing the necessity for
employment of catalysts. These catalysts must be able to reduce NO\textsubscript{x} in net oxidizing conditions. Today’s technologies allow various numbers of possibilities for NO\textsubscript{x} reduction. In general, those can be divided into two main categories; primary and secondary catalytic systems. Primary system is mostly based on catalytic combustion, implying that a part of the air/fuel mixture is reacted heterogeneously over a catalyst before the actual combustion occurs. For these types of catalysts, it is necessary to use premixed combustion which may bring enormous problems regarding liquid fuels, especially for aircraft turbines.

Secondary systems in turn achieve the reduction of NO\textsubscript{x} in the exhaust gas. There are two promising secondary systems for the reduction of NO\textsubscript{x}-emission under lean-burn conditions. One of those is the storage-reduction technology (NO\textsubscript{x}-SR). This technology allows the storage of NO\textsubscript{x} by adsorption on the surface of the catalyst during the lean-burn phase and subsequently, desorption and reduction of the absorbed NO\textsubscript{x} during the following fat-burn phase. Because the second phase is much faster than the storage phase, a significant NO\textsubscript{x} reduction can be achieved in total.

The second promising candidate technology is the selective catalytic reduction of NO\textsubscript{x} (SCR) with addition of ammonia or hydrocarbons as reductant. For stationary systems ammonia is widely used, although for mobile systems hydrocarbons are preferred. As the reductant and NO\textsubscript{x} react over the catalyst, NO\textsubscript{x} is converted to N\textsubscript{2} and O\textsubscript{2} and thus, reduced. The problem regarding the systems working with ammonia addition is the production of non-reacted NH\textsubscript{3} which inflows the environment and/or forms corrosive products. In turn, the hydrocarbons (fuel, kerosene) are more easily applicable on mobile systems.

MnO-doped La-hexaluminate has been suggested as a promising material for the above mentioned catalytic systems. Earlier studies on rare earth lanthanide oxides report high catalytic activity as SCR-catalyst material. With La\textsubscript{2}O\textsubscript{3} and SrLa\textsubscript{2}O\textsubscript{3}, a high conversion of NO\textsubscript{x} with methane is shown with or without oxygen. Due to highly hydroscopic property of La\textsubscript{2}O\textsubscript{3}, its technical realization as catalyst material is difficult, making it necessary to direct the investigations towards finding out more stable chemical compounds of La-oxides for this application.

MATERIALS AND METHODS

Manganese (II) oxide doped lanthanum hexaluminate (LaMnAl\textsubscript{11}O\textsubscript{19}) has been produced by means of two processing routes. Figure 1 shows the procedure for sol-gel synthesis of lanthanum manganese hexaluminate powder. After drying at 200°C, the powder was calcined for 1 hour at various temperatures from 600°C to 1400°C. The detailed synthesis procedure is described elsewhere.

XRD-measurements of the calcined powder were performed with a step size of 0.020° at 20 angles from 10° to 80° on a Siemens D5000 diffractometer using nickel-filtered CuK\textalpha radiation. The samples were characterized microstructurally and compositionally by Energy Dispersive X-ray spectroscopy (EDX) supported Scanning Electron Microscope (SEM Leitz LEO 982). X-ray diffractograms of the used LaMnAl\textsubscript{11}O\textsubscript{19} powder showed that the crystallization to magnetoplumbite phase occurs above 1100°C. Therefore, the powder was pre-calcined for 1 h at 1000°C in order to carry out the FTIR measurements.

The FTIR spectra were recorded on a Bomen MB 102 FT-IR spectrometer equipped with a liquid-nitrogen cooled MCT detector at a resolution of 4cm\textsuperscript{-1}. The detailed setup is described elsewhere.
Beside the sol-gel synthesized powder, EB-PVD (Electron-Beam Physical Vapor Deposition) manufactured LaMnAl11O19 coatings were analyzed. For deposition of coatings, a two-source 150 kW electronic beam coater was used consisting of separated chambers for loading, preheating, and deposition. Ingots which meet the special requirements of the EB-PVD deposition were bottom fed in the crucibles during evaporation to ensure continuous and constant deposition conditions. The substrates were rotated during the vacuum evaporation. SEM, EDX, and XRD-analysis of the EB-PVD coating layers were carried out as described above.

![Diagram](attachment:image.png)

**Figure 1: Sol-gel route synthesis of LaMnAl11O19**

For the catalytic characterization of the hexaluminate coatings, a user-specific and computer controlled experimental setup consisting of a gas-mixer, a tube-furnace, a gas-tight, ceramic specimen holder, and two electrochemical gas sensors from Sensoric GmbH was employed. As carrier gas synthetic air and as test gas nitrogen monooxide (NO) were used. In order to achieve a maximum surface area, a small honeycomb structured component was built by bonding pieces of the layers together. The size of this component was similar to that of the cross sectional area of the specimen holder being about 10 mm long.

RESULTS AND DISCUSSION

Production and Characterization of Materials

XRD-analysis of the sol-gel synthesized MnO-doped La-hexaluminate powder after calcining for one hour at various temperatures up to 1200°C showed that the powder was amorphous up to 900°C and crystallized to the magnetoplumbite phase at about 1000°C. Since the crystallization occurred without the formation of other phase(s) which is mostly encountered in the case of undoped La-hexaluminate, it can be attributed that the formation of the
magnetoplumbite phase at MnO-doped La-hexaluminate is due to a crystallisation process and not due to a reaction between LaAlO₃ and Al₂O₃.

Scanning electron microscopy (SEM) investigation of the sol-gel-synthesized and 1200°C calcined powder shows the formation of hexagonal, plate-like grains with random crystal growth, leading to an interlocking and high surface morphology (Fig. 2). The high surface area of the morphology supports the catalytic effect of the material.

Figure 2: SEM micrographs of sol-gel synthesized and calcined LaMn₃Al₁₁O₁₉ powder morphology on the surface of a particle (a). SEM micrographs of 1100°C heat-treated EB-PVD manufactured MnO-doped La-hexaluminate coating showing the columnar morphology (b); Back scatter image detail of the interlocking microstructure after heat-treatment (small picture at c).

EB-PVD processing of LaMn₃Al₁₁O₁₉ with multiple beam patterns delivered a stoichiometric layer. Since the vapor pressures of individual oxides within LaMn₃Al₁₁O₁₉ composition, i.e. MnO, La₂O₃ and Al₂O₃ exhibit strong differences, EB-PVD manufacturing of this composition requires less power than that of PYSZ evaporation and subsequently leads to lower substrate temperature. Therefore, the as-received EB-PVD coatings were amorphous and a heat-treatment process was needed for its crystallization. SEM micrographs shown in Figure 3 display the columnar EB-PVD-coating (Fig. 2b) and the formation of interlocking plate-like morphology of magnetoplumbite phase after heat-treatment as detected in back-scatter SEM-modus (Fig. 2c).

Magnetoplumbite phase of La-hexaluminate has a highly defective crystal structure, consisting of [AlO₄]²⁺ spinel blocks, intercalated by mirror planes of composition [LaAlO₃]⁶⁺. The introduction of Mn(II), a divalent ion, in the spinel block forms an electrically neutral structure. This promotes the formation of magnetoplumbite phase, with an interlocking needle-like morphology. Once formed, the phase is stable up to 1400 °C.

FTIR-Measurements

The specimen for the FTIR measurements was prepared as described above and activated by heating for 1 h in vacuum, followed by 100 Torr oxygen for 1h and again vacuum for 1 h. All steps were performed at 500 °C.

The FTIR spectrum of the activated sample was recorded at ambient temperatures and taken as a background reference. Each shown spectrum is subtracted by this background reference. On the surface of the activated samples only absorptions in the hydroxyl-stretching-region and the surface-carbonate-region were observed. The weak bands at 3862 cm⁻¹ and 3675 cm⁻¹ are attributed to Al³⁺-OH¹² and La³⁺-OH¹³.
NO was added to the activated catalyst at room temperature for 20 minutes. The addition of NO resulted in an adsorption of NO on the surface which was disproportionate with time. Bands were observed at 1610 cm⁻¹, corresponds to the banding mode of adsorbed water, at 1398 cm⁻¹, identified as NO₂⁺ species, at 1208 cm⁻¹, characteristic for hyponitrite (N₂O₃⁻) and a defused adsorption at 1512 cm⁻¹, which is typical for surface nitrates.

![Figure 3: Temperature controlled vacuum diffraction of adsorbed surface species under NO/O₂](image)

The addition of 60 Torr of oxygen into the reactor (containing 30 Torr of NO) led to great changes in the spectrum. The nitrosyl bands disappeared and the nitrite-nitrate region changed drastically. New bands at 2229 cm⁻¹ and 1752 cm⁻¹ belonging to NO⁺ species and adsorbed N₂O₄ appeared indicating that oxidation of NO took place. The adsorption of NO₂ can occur by disproportionation under the participation of Lewis acid-base pairs and/or surface hydroxyls ¹⁴.

Evacuation of the reactor for 15 min at ambient temperatures resulted only in a few changes in the spectrum, associated to the disappearance of NO⁺ and N₂O₄ bands (Fig. 3). After evacuation temperature controlled diffraction was done. At 100 °C only changes in the shapes and intensities were observed, indicating that a rearrangement of the NO₃⁻-species occurs. Remarkable decomposition of the surface NO₃ species begins at 175 °C (Fig. 3). From the thermal stability and the magnitude of the ν₃ spectral splitting the nitrates bands, it was assigned that monom-, bi- and bridged species form (Fig. 3). The high temperature stable species can be identified as NO₂⁻ species ¹³. Detailed analyses of the desorption process of the surface nitro-nitrate structures are underway, in order to investigate the decomposition to NO and/or NO₂, or to N₂ and O₂.

Adsorption of NO/O₂ for 30 min was repeated and then evacuated for 10 min at room temperature. Than methane (CH₄) was added to the FTIR cell and heated for 15 min at various temperatures (Fig. 5). The heating to 250 °C led to a loss of the adsorbed nitrate species. The subtraction spectrum in Fig. 6B shows a parallel re-adsorption of the adsorbed H₂O (bands 3875 cm⁻¹ and 3675 cm⁻¹). Heating to 350°C for 20 min showed a strong decrease in the nitrite-nitrates bands, accompanied by the adsorption of H₂O (band 1610 cm⁻¹). This indicates that the oxidation of CH₄ took place leading to the formation of adsorbed water. Further increase of temperature up to 450°C for 20 min raised the adsorption of water instead of decreasing. The subtraction spectra showed the formation of a new band at 1372 cm⁻¹ corresponding to bidentate carbonates and negative bands due to the nitrite-nitrate species consumption (Fig. 5B). The changes of the
spectra in the Lanthanum-NO species region could not be observed, due to the spectral bandwidth of the employed FTIR.

Figure 4: Spectra (left) and subtraction spectra (right) of an adsorbed NO/O₂ catalyst surface under CH₄ atmosphere (0.06 bar) at various temperatures

Catalytic Characterization

With the as-received EB-PVD MnO-doped La-hexaluminate layers catalytic experiments were performed. Before performing the catalytic experiments, a dry run with no specimen was carried out in order to examine the operation of the experimental setup. A "background" graph was recorded at several temperatures up to 900°C and with NO concentrations of 25 and 50 ppm at a total flow rate of 400 ml/min. Synthetic air was used as carrier gas, thus there was an oxygen rich atmosphere of about 20% of excess oxygen and a humidity of 50%. The results were reproducible. During background tests, no formation of nitrogen dioxide (NO₂) was detected at any temperature and with all NO concentrations. In turn, it was detected that the measured NO concentration decreases with increasing temperature, assuming that this decrease is either due to adsorption effects at walls of the ceramic holder or decomposition of NO to N₂ and O₂. Relying on these assumptions, all the measured results shown here were corrected by the pre-measured background values.

The experiments were carried out with as-received i.e. amorphous/crystalline layers of EB-PVD manufactured MnO-doped La-hexaluminate. NO reduction and conversion was observed at temperatures 200, 400 and 600 °C. Simultaneously an increase in NO₂-concentration has been detected which was almost compatible to the concentration reduction of NO at the corresponding temperature (Fig. 5). Percentage ratio of NO reduction to the theoretical expected NO concentration seems to depend on the NO concentration and on temperature. The temperature dependence is likely due to the catalytic activity temperature of LaMnAl₂O₉ whereas the concentration dependence is probably to the present surface area of the honeycomb structure. Comparison of the measured concentrations of NO and NO₂ with the theoretically expected
concentrations indicates some negligible deficit which is presumably due to the conversion of the gas to another species, which can not be detected with the present setup.

![Figure 5: Catalytic activity of LaMnAl11O19 EB-PVD layer under NO+synthetic air atmosphere at different temperatures (NO: dotted; NO2: continuous; temperature: dashed). The numbers show the NO reduction in percentage to the theoretical expected concentration](image)

Considering these results and observed FTIR-spectra, it can be presumed that chemisorption of O2 occurs on oxygen defect sites, leading to the formation of charged oxygen species which might promote the formation of NO2 and the adsorption of NOx species on surface sites of LaMnAl11O19. Moreover, it must be noted that the FTIR measurements are carried out under low pressure atmospheres, whilst the catalytic measurements at atmospheric pressure. It is known that thermal stability of the adsorbed surface nitrates increases with pressure which may explain the observed discrepancy between two different experiments. The decomposition of the adsorbed (surface) nitrates to O2 and N2 upon increase of the temperature is not unlikely, although it can not be definitely disclosed. New measurements with a better equipped experimental setup are underway.

CONCLUSION

FTIR spectra show adsorption of NO under oxygen and oxygen free atmospheres. On adsorption of NO at room temperature, surface-nitrates form, most likely as anionic nitrosyl and nitro-species. The adsorbed NO undergoes disproportionation with time involving surface OH groups. Oxygen addition changes the spectrum, mainly due to the oxidation of NO, NO+ and N2O4 surface species. The evacuation leads to the disappearance of NO+ and N2O4 and results in slight changes in the nitrate region of the spectrum. Under vacuum nitrates are stable up to 300°C.

Catalytic characterization of EB-PVD layer of LaMnAl11O19 confirms the promotion of NO-oxidation. The FTIR measurements were carried out under vacuum, It is likely that the decomposition and desorption temperatures under atmosphere pressure differ and are higher from those. Activity temperatures around 700°C under combustion conditions therefore seem to be feasible.

Due to the limitations in bandwidth of the employed FTIR equipment, the behavior of NO species at La-surface sites could not be characterized in order to determine HC-SCR mechanism. Regarding the methane at FTIR spectra in Fig. 5, it can be assumed that the Mn-surface sites
were blocked by adsorbed NO-species which are likely non-reactive towards CH₄. Doping LaMnAlₓO₁₉ with single-oxidation-state ions, like Mg, it may force that the Mn-ion remains in 2⁺-oxidation state resulting in adsorption of NOₐ-species which are more reactive with methane or formation of free active surface-sites. According to previous investigations, NO can be converted over rare earth metal oxide catalysts, especially over La₂O₃, with a high rate to N₂ and CH₄ in the present of oxygen. Therefore further experiments which involve the detection of La-sites and modification of LaMnAlₓO₁₉ by doping with Mg may be eligible.

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REFERENCES
ABSTRACT

This paper presents the latest progress in high porosity filter product development for the 4-way application as well as the corresponding property and performance attributes. Two new compositions, Dev-HP1 and Dev-HP2, at 72% porosity with median pore sizes of 17 μm and 20 μm are identified and under development. From composition development, narrow pore size distribution and good pore connectivity were achieved in comparison to the previous version of high porosity filters, Dev-EC, and also the standard commercial product, DuraTrap® CO. As a result, the pressure drop performance has been significantly improved while a high filtration efficiency of more than 95% has been preserved (artificial soot lab test). The detailed physical property and performance data for these two new 72% porosity filters (vs. Dev-EC and DuraTrap® CO) are discussed. It is anticipated that significantly improved pore microstructure and high wall permeability will allow high catalyst loading in the wall for the 4-way catalyst application.

INTRODUCTION

Diesel engines are the most energy efficient powertrains among all types of internal combustion engines known today. This high efficiency translates to very good fuel economy and low greenhouse gas emissions (CO₂) which helps reduce the global climate effect. Other diesel engine advantages that have not been matched by competing energy conversion machines include durability, reliability and fuel safety. Nowadays, in Europe, about 50% of passenger cars are diesel powered, and this trend is increasing, with a diesel share of new passenger cars in Western Europe at 51.9% [1]. Due to the potentially harmful effects on health and on the environment from both NOₓ and PM (particulate matter) emissions, there is a need for a reduction of these emissions, and the regulations are tightening in Europe, Japan, and the USA [2]. For example, US 2010 regulations require tailpipe emission to be 0.2g/bhp-hr NOₓ and 0.01g/bhp-hr PM for heavy duty applications.
To meet US2010 regulations for both PM and NO\textsubscript{x} emissions, there are several technologies proposed including diesel particulate filter (DPF), NO\textsubscript{x} trap or selective catalytic reduction (SCR) for NO\textsubscript{x}, and their combination. The combination of PM and NO\textsubscript{x} is the most attractive due to expected cost and space saving, but it is also the most challenging technology. Toyota has introduced their first combined PM/NO\textsubscript{x} emission control technology in late 2003 in Europe (Toyota Avensis 2.0L) and in Japan (Hino truck 4.0L), using the diesel particulate and NO\textsubscript{x} reduction (DPNR) catalyst system with NO\textsubscript{x} trap on cordierite filter developed jointly by Toyota, NGK, DENSO et al. [3,4]. With the worldwide tightening regulations, it seems that all diesel vehicles sold in these areas (Europe and Japan) will ultimately have integrated NO\textsubscript{x} and PM functions. Alternatively, selective catalytic reduction (SCR) catalysts can be used to replace NO\textsubscript{x} trap catalysts in a DPF to provide NO\textsubscript{x} reduction. Because such a system is also able to reduce CO and HC emissions through catalytic oxidation, the system is also called 4-way catalyst system. Both NO\textsubscript{x} trap and SCR 4-way systems have their own advantages and drawbacks in catalyst technology and system design. However, their NO\textsubscript{x} reduction performance (efficiency and capacity) is dependent upon the total amount of catalyst loading in DPF filter. A high porosity filter is the leading approach to achieve high catalyst storage. How to maintain the delicate balance between high porosity and thermo-mechanical durability is a challenging problem, and this paper sheds some light on the latest progress in high porosity filter product development.

BACKGROUND

Catalytic converters based on cordierite have been developed and widely used over the past 35 years for the automotive market thanks to a long history of discovery and development [5]. Cordierite is a refractory ceramic with a melting temperature around 1450°C. Another key feature of cordierite is its low coefficient of thermal expansion (typically lower than 4 x 10\textsuperscript{-6}/°C), which explains its excellent thermal shock resistance, an attribute necessary for automotive applications. Similar attributes of cordierite have also been found desirable for diesel particulate filter applications.

MATERIALS AND PROPERTIES

Specific amounts of selected raw materials with carefully controlled particle size distributions are batched together, milled and then extruded to form monoliths, which are then dried and fired with specific schedules, before finally being plugged to make a filter (adjacent channels alternatively plugged at each end in order to force the diesel exhaust through the porous walls acting as a mechanical filter). Figure 1 shows the different processing steps followed to obtain a cordierite ceramic monolith.

Mix Clay + Talc + SiO\textsubscript{2} + Al\textsubscript{2}O\textsubscript{3} Raw Materials
With pore formers and organic binders
\downarrow
Mull, Extrude, Dry
\downarrow
Firing = 1380-1450°C
Figure 1. Generic Processing of Cordierite Monolith

The porosity is controlled during the solid state reaction taking place during firing of the monolith. Higher and more controllable levels of total porosity can be achieved by adding pore...
formers to the batch. By careful material composition development and subsequent drying and firing process optimization, we are able to engineer and control filter pore microstructures and their characteristics in terms of total porosity, pore size and pore size distribution.

Table 1 summarizes the key physical properties for two newly fabricated filters in development, Dev-HP1 and Dev-HP2, in direct comparison to a previous version high porosity filter, Dev-EC, as well as DuraTrap CO, a commercial cordierite filter product. The detailed methods used to measure physical properties of filter materials were described in a previous paper [6].

Table 1. Physical Properties for High Porosity and Reference Filters

<table>
<thead>
<tr>
<th>Property/Composition</th>
<th>DuraTrap CO</th>
<th>Dev-EC</th>
<th>Dev-HP1</th>
<th>Dev-HP2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity (volume %)</td>
<td>50</td>
<td>64</td>
<td>72</td>
<td>72</td>
</tr>
<tr>
<td>Intrusion Volume (ml/g)</td>
<td>0.4</td>
<td>0.7</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>Fine Pore Size at 10% pore filling $d_{10}$ ($\mu$m)</td>
<td>5</td>
<td>5</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>Mean Pore Size $d_{50}$ ($\mu$m)</td>
<td>12</td>
<td>11</td>
<td>17</td>
<td>20</td>
</tr>
<tr>
<td>Coarse Pore Size at 90% pore filling $d_{90}$ ($\mu$m)</td>
<td>35</td>
<td>20</td>
<td>32</td>
<td>37</td>
</tr>
<tr>
<td>d-factor $(d_{50}-d_{10})/d_{50}$</td>
<td>0.58</td>
<td>0.54</td>
<td>0.47</td>
<td>0.50</td>
</tr>
<tr>
<td>Coefficient of Thermal Expansion (CTE) - (RT to 1073 K) (x10³)</td>
<td>3.5</td>
<td>4.8</td>
<td>8.7</td>
<td>7.5</td>
</tr>
<tr>
<td>Modulus Of Rupture- MOR at RT, in MPa (cells per square inch/wall thickness in mil)</td>
<td>2.76 (200/12)</td>
<td>1.67 (200/12)</td>
<td>1.19 (300/13)</td>
<td>1.25 (300/13)</td>
</tr>
<tr>
<td>E-Modulus at RT, in MPa</td>
<td>5.52</td>
<td>2.36</td>
<td>1.08</td>
<td>0.98</td>
</tr>
<tr>
<td>Strain (x10⁻⁶)</td>
<td>5.00</td>
<td>7.95</td>
<td>11.03</td>
<td>12.82</td>
</tr>
<tr>
<td>Thermal Shock Parameter (K)</td>
<td>1429</td>
<td>1657</td>
<td>1267</td>
<td>1709</td>
</tr>
<tr>
<td>Bulk Volumetric Heat Capacity (J/l K)</td>
<td>500</td>
<td>420</td>
<td>346</td>
<td>346</td>
</tr>
</tbody>
</table>

The parameters $d_{10}$, $d_{50}$ and $d_{90}$ are the pore diameters at respectively 10%, 50% and 90% volumes filled by mercury. The d-factor, $(d_{50}-d_{10})/d_{50}$, is used to describe the fine fraction of the pore size distribution (PSD). The coefficient of thermal expansion (CTE) of a material reflects how much this material expands (or contracts) during heating (or cooling). The cell per square inch (cpsi) and wall thickness both indicate the cell geometry of the filter. The mechanical strength is measured by using a four-point bending method, which provides the corresponding modulus of rupture (MOR), or fracture stress. The elastic modulus (E-Mod, or Young’s modulus)
is a way to measure the degree of stiffness of a material. It is commonly known that for brittle materials such as ceramics, the lower the elastic modulus, the lower the stress for a given strain (deformation/elongation).

Pore Characteristics and Microstructures

As shown in Table 1, two new filter compositions, Dev-HP1 and Dev-HP2, were identified that achieve ultra-high porosity of over 70%. This is a substantial increase in porosity compared to previous versions of high porosity cordierite filters which have porosities around 60% [3,4,7] and a commercial cordierite filter product of 50% porosity, DuraTrap® CO. In addition to increased porosity, two distinct median pore sizes at 17 μm and 20 μm were developed for these new filter compositions [7]. The reason why these two median pore sizes were selected was to gain a better understanding as well as a technical evaluation of the catalyst coating response. Moreover, they also enable a deeper understanding of the delicate trade off between pore size and mechanical properties, especially for porosity levels as high as 72%.

In order to refine the filter pressure drop and catalyst coatability, an effort has been made to improve the pore size distribution of these two new filter compositions since the material mechanical strength is limited by the largest pore size, not the median pore size. The d-factor is used to describe the fine fraction of the pore size distribution. The lower the d-factor, the lower the pressure drop and also the better the catalyst coatability expected due to a reduction in the fine fraction of pores. The fine pores are always coated first due to the capillary effect in catalyst coating process and are expected to have a negative impact on back pressure. As listed in Table 1, Dev-HP1 and Dev-HP2 filters have d-factor values of 0.47 and 0.50 respectively, compared to 0.58 for DuraTrap® CO and 0.54 for Dev-EC.

Another important aspect of these two new high porosity filters is the significant improvement in their mercury intrusion volumes. The intrusion volume in a filter is a direct measure of physical space or volume available in the wall for catalyst storage space. There is about a 40% increase in intrusion volume for both new compositions compared to previous Dev-EC, and about 150% increase vs. DuraTrap® CO.

The pore characteristics described above can also be seen in their corresponding SEM pictures shown in Figure 2. It is obvious that both new high porosity filters show better uniformity in pore microstructure and connectivity compared to Dev-EC and DuraTrap® CO filters. Furthermore, the increased median pore size from 17 μm to 20 μm can be observed in the microstructures as well, which will allow higher catalyst loading while preserving a reasonably low back pressure.

Thermal and Mechanical Properties

Both Dev-HP1 and Dev-HP2 are early stage experimental compositions as product concepts. From the preliminary process development to make these two new high porosity compositions into filters, their coefficients of thermal expansion are at 8.7 x 10^-7/°C and 7.5 x 10^-7/°C respectively, which are higher than the reference filters Dev-EC at 4.8 x 10^-7/°C and DuraTrap® CO at 3.5 x 10^-7/°C. Clearly, the coefficients of thermal expansion for both Dev-HP1 and Dev-HP2 preferably need to be decreased to be comparable to DuraTrap® CO.

As the porosity continues to increase, the filter mechanical strength is impacted. As listed in Table 1, the moduli of rupture for the two new high porosity filters are significantly reduced.
Figure 2. Pore Microstructures of DuraTrap® CO, Dev-EC, Dev-HP1 and Dev-HP2

(at 172 and 182 psi respectively, even for the 300/13 geometry) compared to more than 240 psi for Dev-EC and 400 psi for DuraTrap® CO filters (200/12 geometry). It is interesting to note that Dev-HP1 at 17 μm median pore size has nearly identical strength to Dev-HP2 at 20 μm median pore size, presumably due to contributions of its pore size distribution. There is an expected strength gain from catalyst coating, especially for heavy washcoat loadings in the 4-way catalyst application.

The material elastic moduli for the two new filters are also directly related to their porosity and pore microstructures. With an 8% porosity increase from Dev-EC to both Dev-HP1 and Dev-HP2, the elastic moduli have been respectively decreased by 54% and 58%. A similar trend is observed from DuraTrap® CO to Dev-EC with a 57% elastic modulus reduction by increasing the porosity from 50% to 64%. These results show significant lower elastic modulus or reduction in rigidity in the ceramic body for our new high porosity filters and hence provide a better capability to withstand thermal and mechanical stress for the filter application.

Thermal Shock Parameter

In diesel particulate filter applications, the filter needs to be regenerated periodically by burning soot in presence of oxygen to reduce pressure drop resulting from soot accumulation. This regeneration event generates an exotherm temperature and related thermal gradient. Depending on the resulting stress level, this could cause cracking of the filter. Similar rapid heating and cooling cycles also occur in gasoline automotive catalytic converter applications where it is common to use the thermal shock parameter (shown below) to describe the tendency of the product to crack upon such thermal gradients:
From this definition, the thermal shock capability of the filter depends upon the combination of mechanical strength, elastic modulus, and CTE. The lower the CTE and elastic modulus, the higher the thermal shock capability. As depicted in Table 1, both Dev-HP1 and Dev-HP2 show adequate thermal shock capability comparable to DuraTrap® CO and Dev-EC, despite higher CTE and lower mechanical strength. Dev-HP2 shows an even better thermal shock parameter than both DuraTrap® CO and Dev-EC filters. Clearly, this results from the extremely low elastic modulus for this filter. The thermal shock parameter for the Dev-HP1 filter is lower than that of the reference filters DuraTrap® CO and Dev-EC due to its higher CTE. Further improvement in mechanical strength and CTE in composition and process development benefits the thermal shock capability of both Dev-HP1 and Dev-HP2.

FILTER PERFORMANCE

In DPF applications, the most important performance attributes are pressure drop, filtration efficiency, and filter durability. Since the filter durability is a function of service life, and also the two new high porosity filters are in early stage of product concept feasibility demonstration, the durability for these two new filters is not included in this study.

Filter pressure drop performance was conducted in lab test device at ambient temperature with air and artificial soot (Printex-U from Degussa Corporation) [8]. All filters were 5.66" or 0.143 m in diameter and 6" or 0.152 m long. The filter was loaded with artificial soot by aerating the fine soot powder into a compressed air stream. After a specific and controlled amount of artificial soot is loaded inside the filter, the filter is removed, weighed, installed on a cold flow pressure drop rig and tested for pressure drop as a function of flow rate. The filter is then incrementally loaded with greater amounts of soot and the overall process is iterated until reaching the desired soot loading level (generally up to 5 g/l). Pressure drop is typically plotted as a function of soot loading for the highest measured flow rate (356 m³/hr). From pressure drop vs. gas flow rate curves, the filter wall permeability at clean and soot-loaded conditions can be determined.

Filtration efficiency was also measured on the same soot-loading device. Filters 2" or 0.05 m in diameter by 6" or 0.152 m long were used in this measurement. A microdiluter was coupled with a condensation particle counter. These instruments are used in conjunction to dilute the aerosol flow upstream and measure the particles present at upstream and downstream of a particulate filter [8]. The filter is weighed before and after the test. The filtration efficiency of the entire system is determined by comparing the upstream and downstream numbers of artificial soot particles while the filter is in a quasi stationary test operation. The ratio of soot particles that are trapped in the filter over the total soot particles injected leads to the filtration efficiency of the system. For a DPF, it is desired to have such number equal to or greater than 90%.

Soot Loaded Pressure Drop

Soot loaded pressure drop performance for two high porosity filters, Dev-HP1 and Dev-HP2, is shown in Figure 3 in direct comparison to DuraTrap® CO and Dev-EC filters (all of them in the bare state). It is obvious that both new high porosity filters have substantially improved soot loaded pressure drop performance, about 44% reduction vs. Dev-EC and about 60% reduction vs. DuraTrap® CO. This excellent pressure drop performance can be ascribed to the improvement of total porosity, pore characteristics and microstructures as discussed above.
As pore characteristics (total porosity, pore size and distribution, and pore connectivity) continue to evolve, it is interesting to observe that the deep bed filtration mechanism during initial soot loading (<0.5 g/l) becomes less pronounced. This is counter-intuitive, especially for increased median pore size of Dev-HP1 and Dev-HPZ, since enlarged pore size will increase the probability of soot penetrating into the wall. One possible explanation is that overall soot laden gas flow is well distributed through the wall porosity due to good pore connectivity and pore uniformity and hence leading to slower gas velocity. As a small amount of soot penetrates into the wall porosity, it will increase soot loaded wall flow resistance similar to that through surface soot cake layers. As a result, deep bed filtration becomes less pronounced.

Whereas these filters have significantly different soot loaded pressured drop, one can also observe that the difference in clean pressure drop is in comparison relatively small. This can be explained by the fact that the difference in pressure drop across the wall between these different filters in the clean state is somehow masked by other factors also contributing to the total pressure drop (such as channel friction or entrance and exit gas compression/expansion).

![Figure 3: Soot Loaded Pressure Drop for Cordierite Filters](image)

Filtration Efficiency

When both filter porosity and pore size are increased for better catalyst coatability and pressure drop performance, it is always necessary to verify that the filtration efficiency is not compromised. Figure 4 shows filtration efficiency as a function of time for both new high porosity filters vs. Dev-EC. An internal standard filter with 35 μm mean pore size was used as a reference to calibrate and qualify the measurement and test setup. As expected, the standard reference starts at 70-80% efficiency due to its initial large pore size of 35 μm. As soon as soot builds up, the filtration efficiency increases since soot shrinks pore opening. It is obvious that the two new high porosity filters along with Dev-EC filter show excellent filtration efficiency greater than 97%.
Filter Wall Permeability

From the pressure drop measurement, wall permeability can be determined for both clean and soot-loaded conditions. The pressure drop as a function of wall permeability is plotted in Figure 5. As discussed above, clean pressure drop for the filters is dominated by other factors than the filter wall permeability after the permeability reaches a threshold value of about $1 \times 10^{-12}$ m$^2$. DuraTrap® CO is right at that threshold for clean wall permeability. Therefore although Dev-EC and Dev-HP2 are two- and six-times better in wall permeability, the overall clean pressure drop among these filters is not so different (as shown in Figure 4). On the contrary, as the wall permeability is significantly reduced by soot as shown in Figure 5 (data point from same set of filters for soot loaded and clean values), the pressure drop then becomes more sensitive to the difference in wall permeability among these different filters.

Wall permeability is one of the most relevant parameters used to predict pressure drop after catalyst coating. With about a factor of three improvement in wall permeability of Dev-HP2 compared to Dev-EC as well as additional improvement in porosity and pore connectivity, it is highly anticipated that these two new high porosity filters should be able to have high catalyst loadings with coated pressure drops comparable to DuraTrap® CO.

CONCLUSION

The new high porosity filters, Dev-HP1 and more particularly Dev-HP2, show a significant improvement over the existing cordierite product, DuraTrap® CO, and also the first generation of high porosity cordierite, Dev-EC. These filters have a total porosity of 72% with narrow pore size distribution and mean pore sizes of 17 μm (Dev-HP1) and 20 μm (Dev-HP2). These basic product attributes are highly desirable for high washcoat loading necessitated for the 4-way application while retaining low soot loaded pressure drop as well as a reasonably low CTE and an acceptable mechanical strength.

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Figure 5. Pressure Drop as a Function of Filter Wall Permeability for Clean and Soot Loaded (4g/l) States

REFERENCES