

Catalytic Nano-structured Materials for Next Generation Diesel Particulate Filters

Souzana Lorentzou, Chrysa Pagkoura,
Alexandra Zygogianni and Georgia Kastrinaki
CERTH/CPERI

Athanasios G. Konstandopoulos
CERTH/CPERI/Aristotle University

Copyright © 2008 SAE International

ABSTRACT

The increasing need for controlled diesel engine emissions and the strict regulations in the abatement of diesel exhaust products lead to an ever increasing use of Diesel Particulate Filters (DPFs) in OEM applications. The periodic regeneration of DPFs (oxidation of soot particles) demands temperatures that rarely appear during engine operation. It is therefore necessary to employ direct or indirect catalytic measures. In the present work, the development and synthesis via aerosol-based routes, of nanostructured base metal oxides for direct soot oxidation, along with their characterization and their evaluation in engine exhaust is described. The synthesized powders were characterized with respect to their phase composition and morphology. XRD, SEM and TEM analysis have shown the nanostructured character of the powders, while Raman spectroscopy was employed for the preliminary characterization of the materials surface chemistry. The catalytic activity of the materials on soot oxidation was evaluated via thermogravimetric analysis (TGA). It was found that they have increased soot oxidation activity at lower temperatures than materials synthesized through a liquid phase route (Liquid Phase Self-propagating High temperature Synthesis, LPSHS). Powders with best catalytic activities were deposited on porous filter structures and were subsequently tested on an engine bench for the evaluation of their catalytic activity under realistic conditions.

INTRODUCTION

The automotive industry is focusing in the development of Catalytic Diesel Particulate Filters (CDPFs) that would collect the soot particles and would accelerate their direct oxidation at the prevailing exhaust conditions. Such catalysts are typically based on base metal oxides [1].

In the current work, the materials investigated for direct soot oxidation were perovskite type catalysts as well as cerium based mixed oxides. In the case of the latter an investigation of the effect of doping on the activity of cerium oxide was performed. It is well known in the literature that doping of cerium oxide enhances the soot oxidation activity of the material due to increase in the defects and in the oxygen vacancies inside its lattice [2].

The synthesis of several groups of materials (namely perovskites designated here as A, B and C as well as cerium-based oxides) was conducted by three different methods. Perovskite A was synthesized via a Liquid Route (LR) while perovskites B, C and cerium-based oxides were synthesized via Liquid Phase Self-propagating High temperature Synthesis (LPSHS) [3]. All of the above materials were synthesized via Aerosol Based Synthesis (ABS) [4-6].

Characterization of the catalytic materials was conducted by employing X-ray diffraction (XRD), Scanning Electron Microscopy (SEM), Transition Electron Microscopy (TEM) and Raman spectroscopy. The catalytic activity of the materials was evaluated via Thermogravimetric Analysis (TGA). The best formulations were deposited on filters via Aerosol Based Deposition (ABD) and were subsequently tested under realistic conditions in an engine test cell bench.

EXPERIMENTAL

SYNTHESIS ROUTES

The synthesis methods employed metal nitrate precursor solutions. In the case of the LR method the synthesis of perovskite A involved calcination at high temperatures (1000 C). An investigation of the effect of grinding of the produced materials on the soot oxidation activity of perovskite A was conducted by grinding the as-synthesized material 1, 6 and 12h.

For the synthesis of perovskites B and C and of cerium based mixed oxides via the LPSHS and ABS methods aqueous solutions of metal nitrate salts, with addition of citric acid – to avoid precipitation of the reactants- and ammonia, were employed. LPSHS is based on spontaneous combustion of the solution due to the formation of explosive ammonium nitrate, which is a product of the reaction of the nitrate ions with ammonia. With moderate heating, ammonium nitrate dissociates violently and produces a high temperature front that propagates helping the metal ions to react with oxygen and produce the metal oxides. All the products synthesized via LPSHS were fired at 700 C for 4 h. Alternatively, mixed oxides were synthesized with ABS, a method during which a solution of the appropriate precursors is atomized. The produced droplets (~2 μm mean diameter) pass through a heated tube reactor, where evaporation of the solvent, precipitation of the solutes and reaction in the solid phase take place and the particles that are produced are collected on a glass fiber filter.

CHARACTERIZATION

X-Ray Diffraction (Siemens D500/501), Scanning Electron Microscopy (JEOL JSM-6300) and High Resolution Transmission Electron Microscopy (JEOL JEM 2010) were employed for the characterization of the materials synthesized as above.

The evaluation of the catalytic activity of the produced powders with respect to soot oxidation was conducted with thermogravimetric analysis. Mixtures of the produced oxides with soot at a ratio of 2:1 on a mass basis were placed in a thermogravimetric analyzer (Perkin Elmer Pyris-6 TGA) and heated under 20% O₂ in N₂ with a temperature increase rate of 3 C/min from 150 up to 700 C.

The Raman spectra of the powders were recorded in the 100-3200 cm⁻¹ region using a micro-Raman (Renishaw inVia Reflex) Spectrometer equipped with an air-cooled Argon ion laser, a CCD detector and an automatic X-Y-Z stage. A 514.5 nm (delivering ~7.5 mW) laser line was used as an excitation source. The synthesized samples were examined at room temperature. For the in-situ investigation of the oxidation reaction between catalyst and soot, a water-cooled high temperature (up to 1500 C) programmable cell was employed. The catalyst-soot mixtures were placed in the heating cell and the measurements were conducted under a flow of air (100ml/min) with a temperature increase from 25 to 700 C at 3 C/min. Backscattering illumination and collection of the scattered light were made through a Leica confocal microscope (long focus Leica x 50 objective, total magnification x 500). The diameter of the laser spot on the sample surface was 1 μm for the fully focused laser beam and 40 μm for the fully defocused laser beam at 50x objective magnification. The acquisition time was 10-60 s and about 5 spectra were recorded for each sample. The soot spectra of highest quality and

reproducibility were generally obtained with laser beam powers of 50%, exposure time of at least 60s and after 3 accumulations. Band position, band intensity (i.e. band height), band area (i.e. integrated area) and band width (i.e. Full Width at Half Maximum, FWHM) were determined using the Renishaw program Wire 2.0. Gaussian-Lorentzian curves are simultaneously fitted to the spectra of soot, in order to model the G, D₁, D₂, D₃ and D₄ bands, as illustrated in Figure 1 [7-9]. The characteristics of the fitted curves, such as height, area, width and lineshape (Gaussian, Lorentzian or mixed) were obtained.

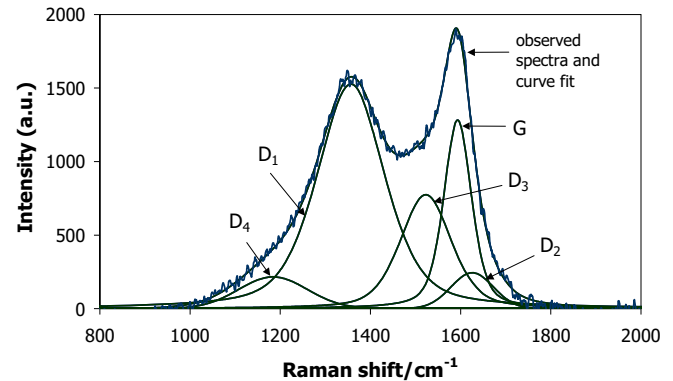


Figure 1: Curve fit for the first-order Raman spectra of soot.

The Raman spectra of soot can be divided into areas of first-order (<1800 cm⁻¹) and second-order (2200 – 3400 cm⁻¹) peaks [10-12]. The bands appeared at this region were the G ("Graphite") band at around 1580cm⁻¹ which is attributed to the natural vibration mode of the six-member ring planes in the graphite structure [13], as well as the bands around 1150, 1350, 1500 and 1620 cm⁻¹ (Figure 1). The 1350 cm⁻¹ band (D₁ band), commonly called the defect band, is the most important feature. This band is attributed to a graphitic lattice vibration mode with A_{1g} symmetry and is known to be characteristic for disordered graphite and to grow in intensity relative to the G band with increasing degree of disorder in the graphitic lattice [14]. Finally, the 1620 cm⁻¹ band (D₂) makes a shoulder on the G band, and is always present when the D₁ band is present [7,15], and its intensity decreases with the increasing degree of organization. In the present work the first-order D₁ and G peaks were studied. The I_{D1}/I_G ratio is characteristic for the degree of structural organization. In particular, increase in this ratio is associated with an increased degree of structural disorganization [16].

The peak intensity ratio between the D and G bands is inversely proportional to the crystallite dimension of graphite. In particular, the crystallite size of graphite is related to this ratio using

$$I_{D1}/I_G = C * l/L_a \quad (1)$$

where C is approximately 4.4 nm (in the case of using 514.5 nm Ar ion as an excitation source), l is the

intensity of D_1 peak, I_G is the intensity of G peak, and L_a is the in-plane crystallite dimension [17].

EVALUATION ON ENGINE TEST CELL

For the investigation of the oxidation activity of the materials under realistic conditions, perovskite A, C and the best formulation of the cerium based catalyst were deposited upon ceramic wall-flow monolithic segments by employing the Aerosol Based Deposition (ABD). The filters used had the same cell density and pore structure. With the ABD process the synthesis and deposition of the catalysts on the porous materials was conducted in one step [18-20]. The coated porous materials were evaluated with respect to their direct soot oxidation activity on a common rail diesel engine with a 1.9 L displacement operated at steady state and coupled to a hydraulic bolt-on dynamometer [21 -23].

RESULTS

PEROVSKITE TYPE CATALYSTS

X-ray diffraction

Perovskites denoted here as A, B and C were synthesized via LR, LPSHS and ABS. As illustrated in Figure 2 perovskite A synthesized by ABS is amorphous while the material synthesized via the LR is well crystallized.

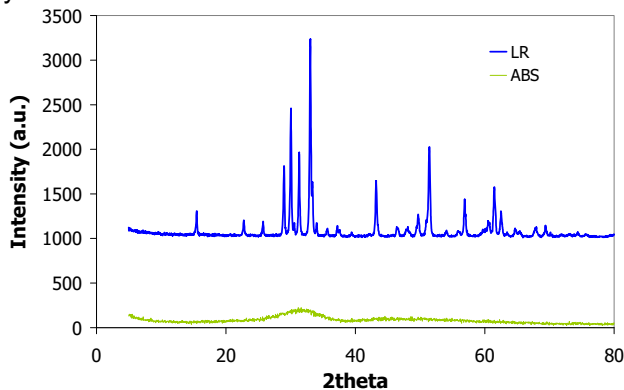


Figure 2: XRD of perovskite A synthesized via LR and ABS.

In the case of perovskites B and C the ABS synthesized materials have the same crystal phase with those synthesized via the LR but again the degree of crystallinity is very low (Figure 3).

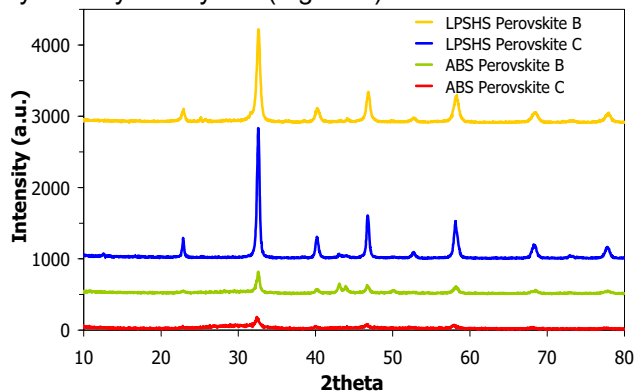


Figure 3: XRD of perovskites B and C synthesized via LPSHS and ABD.

TGA experiments

In Figure 4 the soot oxidation rate as a function of temperature for the case of perovskite A is depicted. It is observed that ABS synthesized material reduces the soot oxidation temperature compared to the LR synthesized catalyst (Figure 4). This could be attributed to deficiencies that may exist in the ABS material due to its amorphous (nanocrystalline) structure.

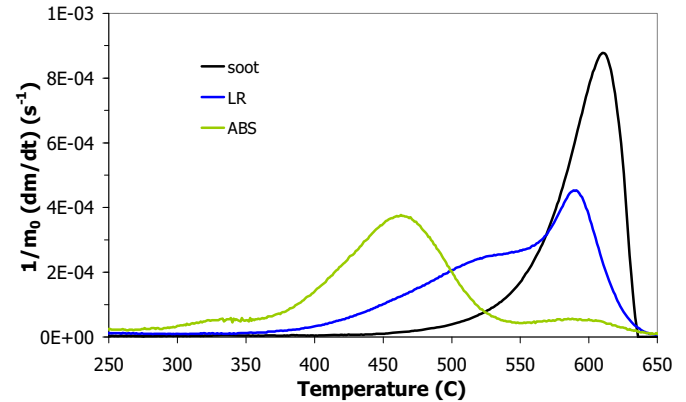


Figure 4: Soot oxidation activity of perovskite A synthesized via LR and ABS.

The effect of the decrease in the catalyst particle size on the soot oxidation activity of the LR synthesized perovskite A was investigated by grinding in a ball mill the as-synthesized material for 1, 6 and 12h. As it can be observed in Figure 5, grinding of perovskite A for 1h shifts the soot oxidation rate curve to lower temperatures. This shift transferred the activity of the LR synthesized perovskite A at similar temperatures with the ABS material. Further grinding did not appear to have any effect on the activity to soot oxidation.

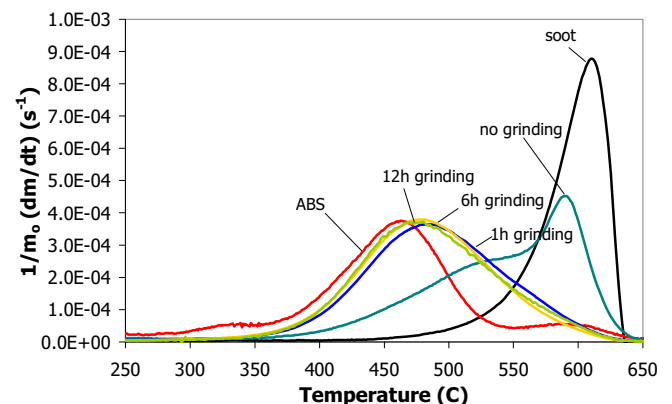


Figure 5: Effect of the grinding on the soot oxidation activity of perovskite A synthesized via LR compared to ABS material.

This effect can be attributed to the decrease in the particle size of the as synthesized material.

In the case of perovskites B and C soot oxidizes at lower temperatures for the C perovskite. The difference between ABS synthesized and LPSHS synthesized