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Catalysis Today 105 (2005) 537–543

www.elsevier.com/locate/cattod

Testing molten metal oxide catalysts over structured ceramic substrates for diesel soot oxidation

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Abstract

Onboard tests of an oxide (CoO_x) and a molten mixed oxide catalyst ($CoPbO_x$) supported on cordierite wall flow filters (Corning Durotrap CO EX80) were performed on rollers with a 1.9-l light duty vehicle for three different driving conditions including two constant speeds with different loadings and a standard European cycle (NEDC). The balance point temperatures obtained in these tests were used to compare the catalytic activity under onboard conditions with laboratory measurements. Onboard tests showed similar catalytic activities with the previous micro-reactor experiments performed in ''loose contact'' mode [D. Uner, M.K. Demirkol, B. Dernaika, Appl. Catal. B: Environ., in press]. The concentration profiles of the active layer determined by SEM-EDX analysis after use and after aging revealed that the mobile component, PbO_x, migrated in the flow direction and accumulated at the closed end of the channel. There is no direct evidence for the evaporative loss of PbO_x. Regions of high activity indicated by low carbon amounts with unique Pb–Co ratios were determined by SEM analysis.

Keywords: Oxidation catalysis; Diesel soot; Mixed oxides; Molten catalysts; Eutectics

1. Introduction

Due to the adverse health effects, particulate matter (PM) emissions from the exhausts of diesel vehicles are now subject to stringent limits [1]. Use of catalytic diesel particulate filters (DPF) for PM emission control has been the subject of intensive research [2,3]. Many candidate catalysts were proposed for catalytic regeneration of these filters including molten catalysts [4,5] and transition metal oxides [6,7]. Molten metals and eutectic salts were proven to be very active diesel soot oxidation catalysts due to the extensive contact they provide during the oxidation process. In spite of the high activity of these materials, the stability and durability issues need to be resolved. The primary durability issue of a molten catalyst is its high volatility inherent in its lower melting points. It is imperative that the molten catalysts are not used in packed bed structures and should be supported on ceramic substrates of regular or sponge structure. The ceramic structures add to the mechanical strength of the catalysts, but on the other hand, the extra surface areas provided by the substrates may enhance their loss via evaporation. Furthermore, some new phases can be formed with the interaction of the catalyst and the support during high temperature operation, which causes degradation in the catalytic activity and/or in the mechanical strength of the substrate as both observed by van Gulijk et al. [8].

Among structured substrates, foam filters were mostly utilized for molten catalysts [4,5,8,9] since the wall flow type filters having smaller pores were speculated to be blocked by the molten phase during operation [8]. Also, these filters cause less back pressure in the exhaust making them more viable for a possible application. Nevertheless, the wall flow filters' advantage of having much higher particulate abatement efficiency with a tolerable back pressure during operation is the reason why they are employed in vehicle applications.

In this paper, engine tests of a thoroughly tested mixed oxide catalyst developed in our laboratories [10] containing

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doi:10.1016/j.cattod.2005.06.018

oxides of Pb and Co were performed after the catalyst was wash-coated on a ceramic wall flow type DPF.

2. Experimental

2.1. Preparation of the active filter

A commercial cordierite DPF (Corning DPF EX-80; 14 cm (D) × 15 cm, 100 cpi, 0.017 in. wall thickness, 48% porosity and mean pore size of 13 μm) was used as a substrate for the catalysts. Before the introduction of the active layer, the filter was cleansed with a surfactant in an ultrasonic bath for 3 h. This procedure helped remove any organic contaminant present on the surface. The filter, then thoroughly rinsed in ultrasonic bath, placed in 1 M HCl, again in an ultrasonic bath for 1 h, washed thoroughly and dried. In order not to cause any cracks inside the filter during drying, the filter was kept in an oven at 70 °C for 2 h and then left to dry overnight at 110 °C.

The slurry that will be used in coating the filter was prepared to have a Pb:Co stoichiometry (w/w) of 2:1. Two different precursors were used as active metal source. A CoO_x (Egeferro) powder, used in production of black paint in the paint industry, was used as the cobalt source. Analytical grade lead acetate tri-hydrate precursor (Riedel-de Haen) was used as the lead source. The precursors were dissolved in distilled water at 55 °C and kept inside ultrasonic bath for 2 h in order to sustain the suspension. Then, the slurry was poured slowly through the channels of the filter from one side. During this process, the filter was kept inside the ultrasonic bath inside a dry container so as to drive the air molecules imprisoned between the slurry and the dead end of the channel. When all the solution was consumed, the filter was taken out of the ultrasonic bath, the excess amount of solution was flushed away by pressurized air and the resulting filter was left overnight for drying. Filter was then dried at 110 °C for 3 h. The dried DPF was calcined in a temperature programmed oven. The temperature of the oven was increased from 25 °C to 450 °C in 1 h, kept at this value for 3 h and cooled down to room temperature. The details of three different filters prepared as described above are given in Table 1.

2.2. Characterization

The active catalyst loading and surface composition profile was analyzed with a scanning electron microscope (SEM, JEOL JSM 6400) equipped with an energy dispersive X-ray (EDX, NORAN system 6) probe. This measurement was performed only on the PbO_x/CoO_x filter. After the onboard tests, SEM samples were cut out of the filter at several locations as shown in Fig. 1. These points were chosen to determine the active material distribution along the channel (axial) and between the channels (radial).

Table 1
The details of the coated filters

Filter	Loading (g/l)	Filter details
Uncoated	N/A	No catalyst coated
CoO_x	46	Mono-coated (CoO_x) filter
PbO_x/CoO_x	102	PbO_x coated over CoO_x sequentially
$PbCoO_x$	98	PbO_x and CoO_x coated simultaneously

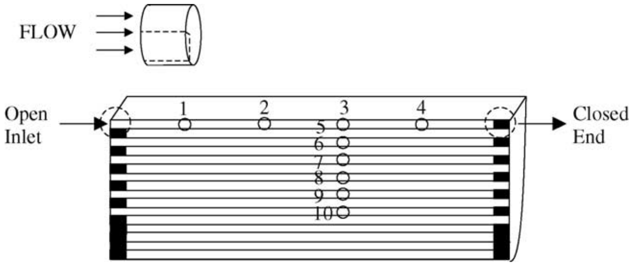


Fig. 1. The locations of the points where SEM and EDX analyses were performed.

2.3. Vehicle onboard tests

The coated filter was then mounted on the exhaust stream of a light duty vehicle equipped with 1.9-l turbocharged Euro-1 diesel engine (see Table 2 for details) by means of a canister. The filter was placed inside the canisters in a kaolin wool blanket. This kaolin wool protected the filter against the mechanical vibrations and provided thermal isolation. Thermocouples (K-type NiCr-Ni) were placed before, after and inside the filter through the holes on the canister and connected to a data acquisition/storage device (Squirrel Meter/Logger 1000 Series). Also, two pressure sensors (EGR Sensors-Bosch PSB-2) were connected upstream and downstream of the filter to monitor the pressure drop caused by the filter. These sensors were connected to data acquisition/power supply device (Datron) and digital signals from this device were transferred to a laptop (Panasonic Tough Book P3 400 MHz) by a serial cable. A software (Windalo T.E.S.T. Version 1.00.05) was used to receive and store the data.

After the filter was placed inside the canister, the assembly retrofitted to the exhaust and the vehicle was placed onto the rollers connected to a dynamometer (Schenck) inside the Test and Emission Laboratory of R&D Department in TOFAS-FIAT Automotive Factory (see Fig. 2). Through the rollers a desired amount of load could

Table 2
Characteristics of the light duty vehicle used in the tests

Vehicle	Fiat Doblo Cargo
Gross weight	1310 kg
Engine	Fiat 1.9 JTD, 1910 cm^3 common rail, Unijet direct injection, turbocharger and intercooler
Maximum power	77 kW/4000 rpm
Emissions	Euro-1 engine, no oxidation catalyst

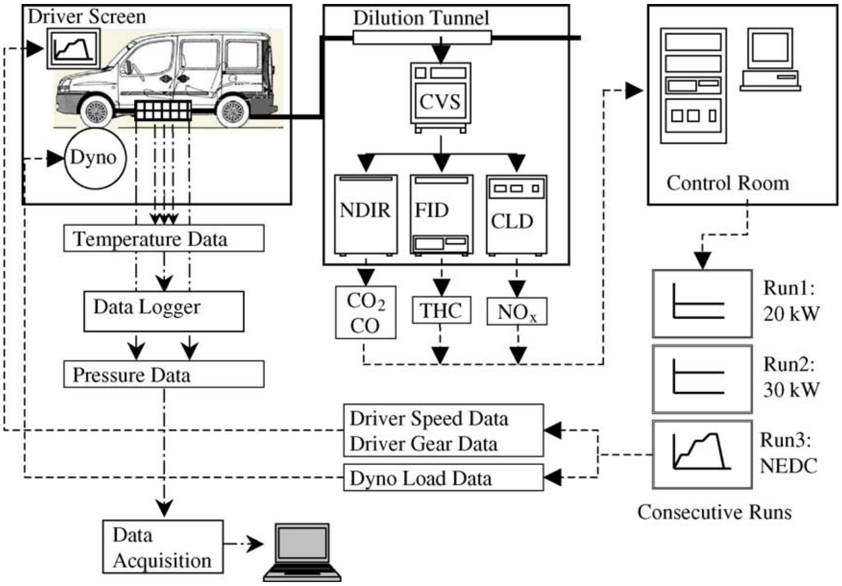


Fig. 2. The flowchart of the onboard tests performed in the Test and Emission Laboratory of TOFAS-FIAT Automotive Factory.

be applied to the wheels. The driver monitored the speed and gear through a computer screen. The speed of the car was monitored through the rollers and sufficient amount of air corresponding to the vehicle speed was blown with a fan placed in front of the car in order to have the same convective conditions in the engine as the real driving.

Exhaust stream of the car was connected to a set of gas analysis devices (Horiba VETS/7000 Test Cell) through a dilution tunnel. The exhaust gases then passed through a set of conditioned absolute filters which filter the PM in the exhaust stream. The weight changes of the filters during each run were determined after conditioning the filters in the same manner. This change in weight gives the PM emission of the vehicle. The gases passing through the filters were then sampled by constant volume sampler (CVS) and fed to a series of gas analysis devices consisting of a flame ionization detector (FID) for total hydrocarbon (THC) emissions, a chemo luminescence detector (CLD) for NO_x emissions, a magnetic paramagnetic analyzer and a non-dispersive infrared (NDIR) for CO and CO_2 emissions. In situ amounts of NO_x, CO_2, CO and THC present in the exhaust gases were determined in this manner and recorded with the speed data. Experiments at two different loadings were performed successively without taking out the filter for regeneration between each run, details of which are given in Table 3. The load on the rollers was chosen to simulate two different driving conditions: a typical driving condition (normal load) and a heavy duty driving condition (heavy load). The fuel used throughout all the experiments was Total Eurodiesel (350 ppm sulfur).

Table 3
The details of vehicle onboard tests

	Speed/gear/rpm	Loading (%)
Normal load	90 km/h, fourth gear, 2650 rpm	38
Heavy load	90 km/h, fourth gear, 2650 rpm	57

2.4. Aging

Also, an aging procedure of 18 h (1600 km) duration was applied for the PbO_x/CoO_x coated filter in order to determine the catalytic activity loss during harsh conditions. Aging was performed on an engine testing bench. The canister containing the filter was placed on the exhaust stream of an identical engine which was connected to a dynamometer. The loading setting was chosen to be 20 kW (normal loading) corresponding to an exhaust temperature of about 325 °C which was below the catalytic regeneration temperature for the PbO_x/CoO_x coated filter (370 °C). This temperature was chosen intentionally to have little regeneration on the filter and therefore cause the accumulation of soot. During aging, the pressure drop and temperature data were collected. After aging, the canister was removed

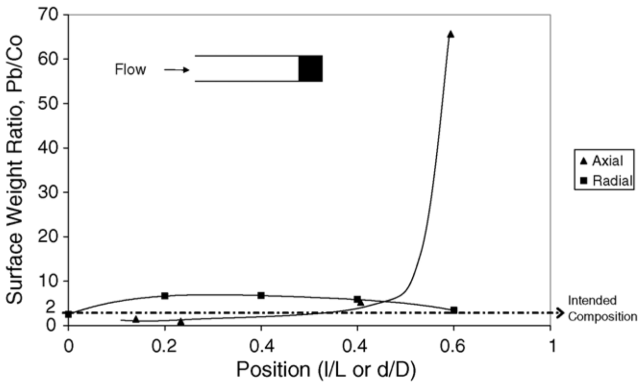


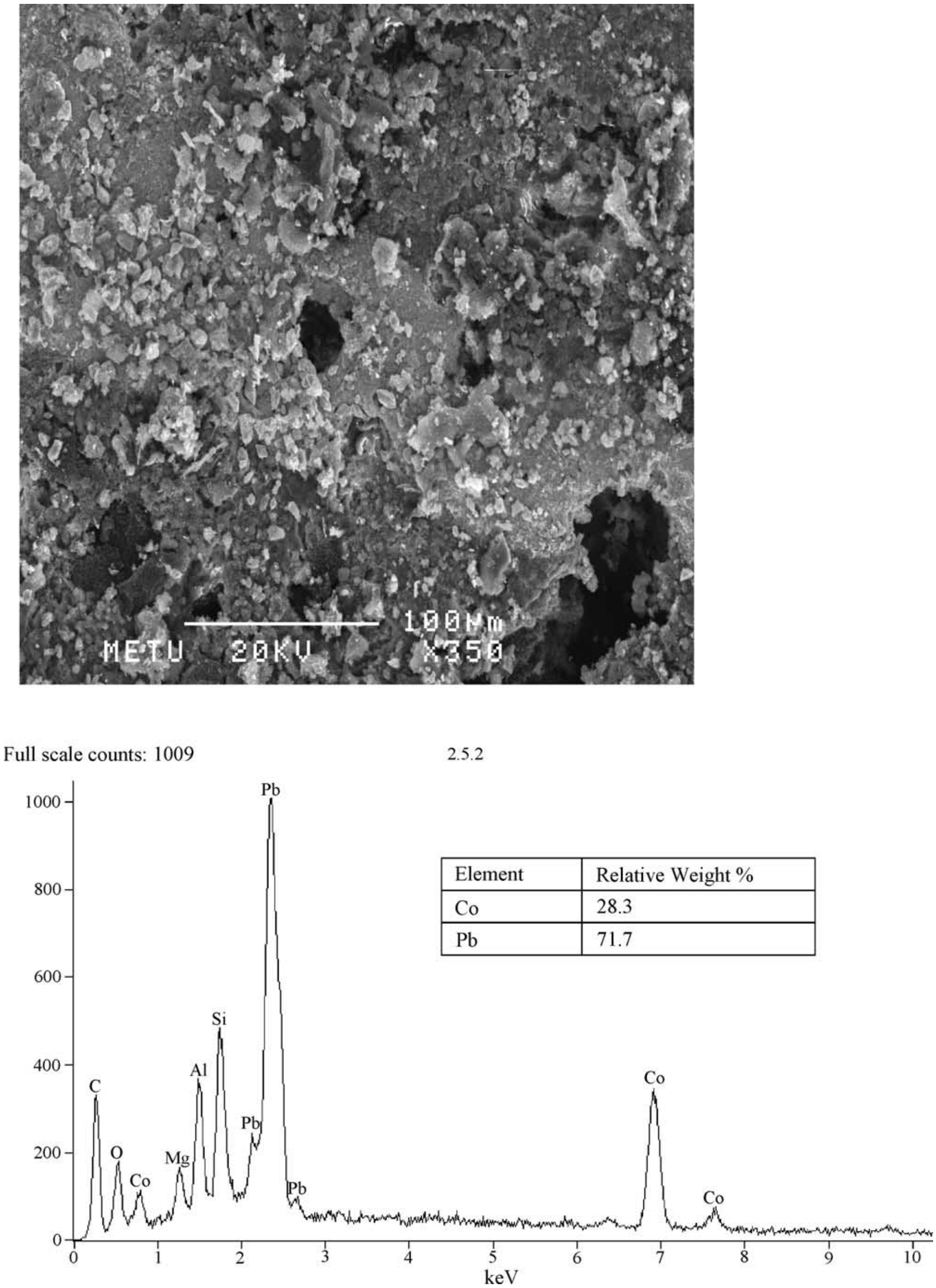
Fig. 3. The surface distribution of the active components as revealed by EDX analysis.

again and placed on the vehicle. The vehicle was then driven on the rollers at heavy load to see the catalytic activity and regeneration of the accumulated soot.

3. Results and discussion

3.1. Characterization

EDX analysis was performed on various points on the filter to determine the active metal distribution along the filter. The results of this analysis are presented in Fig. 3. For the ease of presentation, the positions where the analyses were performed were expressed in terms of the ratio of the distance from the inlet (l) to the total length of the filter (L), and ratio of the distance from the centerline of the filter piece (d) to the diameter of the filter (D), for the axial and radial distributions, respectively. For the channels considered, the metal loading inside the channel showed a large variation from the front to the end: the weight percent of Pb was increasing along the flow direction of the channel whereas the Co percent was decreasing. This distribution was



Element	Relative Weight %
Co	28.3
Pb	71.7

Fig. 4. SEM image and the EDX analysis plot of one of the eutectic areas on the filter (point 10 of Fig. 1) recognized during imaging.

interpreted to be due to accumulation of the evaporated Pb molecules at the closed end of the channel. Cobalt and its oxides are not susceptible to evaporation due to their high melting points during the onboard experiments where a maximum of 450 °C was reached. On the other hand, lead and one of its oxides (PbO_2) have lower melting points than this temperature and they possess much higher volatility than cobalt. The radial distribution of the active phases did not show much variation as that of the axial distribution. It is also important to note here that the measured composition at almost all of the points were two to three times larger than the intended composition as shown by a dashed line in Fig. 3. The variation of the radial composition as well as axial composition is indicative of the mobility of the active phase of the catalyst which needs to be stabilized.

During the SEM imaging of the filter walls, some extraordinary areas, such as shown in Fig. 4, were recognized having no dark soot layers accumulated over them, indicating a better soot oxidation activity. These areas were further analyzed with EDX to identify the surface concentration. The peak intensities of the active metals (Co and Pb) were much higher relative to the measurements taken at other positions of the filter. On the contrary, the carbon peak was much smaller. Furthermore, the characteristic Mg, Si, Al and O peak pattern of the cordierite filter was also apparent, implying the absence of the thick soot layer hindering the filter surface. The surface composition of this area in terms of active metals were integrated and given on the EDX patterns. This composition is suspected to be the eutectic composition of Pb and Co since it exhibited an extra stability with its high Pb content and showed an exceptional soot oxidation activity. The EDX analysis result of the eutectic areas and the integrated relative weight percents of the active metals are also given in Fig. 4.

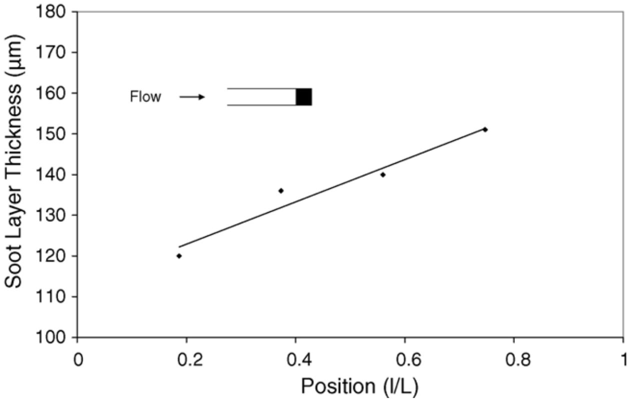


Fig. 5. The thickness of the soot layer along the channel as measured by SEM-EDX.

Using the cross-sectional SEM images of the filter walls, the thicknesses of soot layer accumulated on the filter walls along the channel were measured and plotted in Fig. 5 in order to identify the nature of soot deposition in the exhaust conditions. As expected, the soot thickness increased going from inlet to the dead end of the channel. Furthermore, the average thickness of the soot layer was about 135 µm which is in the intrusion range of EDX analysis.

3.2. Vehicle onboard tests (determining the balance point temperature)

During the roller tests, the pressure drop caused by the filter was monitored in order to observe the amount of soot

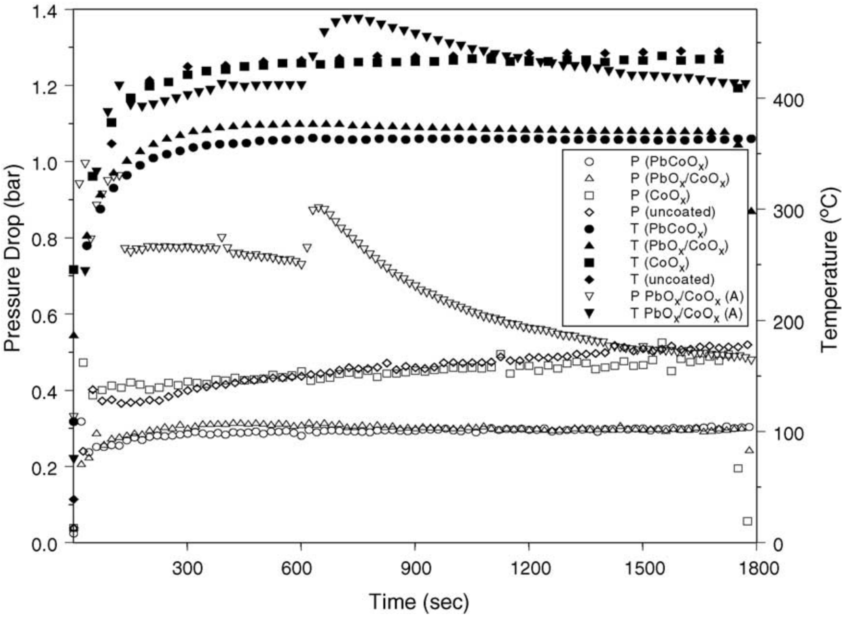


Fig. 6. Pressure drop (empty symbols) and filter temperature (filled symbols) profiles obtained in heavy load (30 kW) constant speed tests. PbO_x/CoO_x (A) data correspond to the heavy load testing of the sample aged for 18 h at the exhaust of a diesel engine under 20 kW load.

accumulated on the filter. Obviously, the flow through the walls of the filter is blocked by the filter pores, catalytic material coated on the filter and the unburned soot particles accumulated on the filter. The cumulative effect of all these constituents is a pressure drop across the filter. For the case of constant mass flow in the exhaust (i.e. constant rpm and load) the only constituent that changes during time is the pressure drop caused by the soot accumulated on the filter. Therefore, the increase in pressure drop during the constant speed experiments was attributed to the accumulation of these unburned soot particles on the filter. The pressure drop profiles obtained under heavy load constant speed tests are presented in Fig. 6. The pressure drop profiles in the figure are nearly linear, except for the first minutes of the tests where the filter encounters unsteady state exhaust temperature and soot production rate. For the case of constant exhaust mass flow rate, the soot production is constant and the amount of soot accumulated on the filter is the difference between the soot produced and the soot burnt. Hence, the slopes of the pressure drop profiles can be used to determine the relative soot accumulation rate on the filters. A good catalyst should yield a zero slope, since this implies that the soot production rate is equal to the soot oxidation rate. Obviously, a negative slope indicates regeneration on the filter.

Consequently, in order to compare the soot oxidation rates, the slopes of steady state parts of the pressure drop profiles (i.e. of the last 10 min of the tests) were calculated and given in Table 4 with the corresponding average filter temperature values in that time interval. Looking at the slopes, the normal load test of CoO_x filter has the highest slope. Actually, the uncoated filter was expected to have the highest slope since there was not a catalytic soot oxidation on this filter. This phenomenon was attributed to the decrease in the porosity of the filter as a result of the catalyst layer on the filter. Due to this extra layer, the small soot particles that can easily pass through the larger pores of the uncoated filter can be collected and therefore contribute to the pressure drop. This hypothesis is verified by the PM emissions of the tests given in Table 4. As expected, the CoO_x filter has a lower emission value than the uncoated filter. When heavy load test was applied to the CoO_x filter after the normal load test, it was observed that the soot accumulation rate was lower for CoO_x filter than that of the uncoated filter, indicating a catalytic soot oxidation at the temperature of testing (i.e. 440 °C). Even though the catalytic soot oxidation was observed at 440 °C, the rate was not enough to compensate the soot production rate as indicated by the positive slope of the pressure drop curve.

Table 4
Slopes of last 10 min of the pressure drop profiles and average temperature and PM emission values for the corresponding tests

Filter	Slope × 10^6 (bar/s)	Average temperature (°C)	PM emissions (g/km)
Normal load			
Uncoated	56	346	0.011
CoO_x	69	347	0.001
PbO_x/CoO_x	38	316	0.005
$PbCoO_x$	22	301	0.014
Heavy load			
Uncoated	73	438	0.024
CoO_x	43	433	0.011
PbO_x/CoO_x	−16	373	0.008
$PbCoO_x$	9	363	0.013

Table 5
Comparison of combustion and regeneration temperatures of the laboratory study and the onboard tests

	Peak temperatures obtained in the laboratory tests (°C) [10]	Onboard tests, T_{bal} (°C)
CoO_x	430	440
PbO_x/CoO_x	385	375
$PbCoO_x$	385	365
Pt-$PbCoO_x$	356	N/A
Uncoated	520	N/A

The PbO_x/CoO_x and $PbCoO_x$ filters showed similar behaviors in both normal and heavy load tests by means of pressure drop profiles and average temperature values. Both filters exhibited a flat pressure drop profile at about 370 °C in heavy load tests indicating a balance between the soot production rate and catalytic soot oxidation. Comparing the two test groups, namely the normal and heavy load tests, the lowest slope, i.e. maximum soot oxidation, was achieved in the heavy load testing of the PbO_x/CoO_x filter with a negative slope indicating regeneration. Both PbO_x/CoO_x and $PbCoO_x$ filters can be declared successful in simultaneous soot oxidation at about 370 °C since there is a little difference in their catalytic activity.

The temperatures, at which flat profiles were obtained (i.e. the soot production rate is equal to the soot oxidation rate), were recorded as balance point temperatures T_{bal}. This temperature was used for comparing the catalytic activity of the supported catalyst with that of the powder form tested in the laboratory, i.e. T_{peak} (Table 5). The results of the engine tests are consistent with previous laboratory experiments in which the catalyst soot mixtures were prepared to resemble a ‘‘loose contact’’ mode [10].

3.3. Aging

One of the filters that were proved to be successful in catalytic regeneration in constant speed tests, namely PbO_x/CoO_x filter, was subjected to aging/filling stage in order to determine the catalytic activity loss after harsh condition driving. After the aging period, the filter was placed back on the vehicle and a power check was performed to determine the power loss of the vehicle caused by the back pressure. This check revealed a loss of 60% in the produced power of the vehicle indicating that the filter was filled thoroughly with soot particles.

The pressure drop and filter temperature profiles obtained on the aged catalysts are also given in Fig. 6. The driving cycle for this catalyst during the emission tests were chosen such that in the preconditioning period the ignition of the accumulated soot was inhibited by driving at a lower speed. This period corresponds to the initial 600 s where pressure drop and temperature profiles are nearly flat. When the gas analysis period started the vehicle was driven at 90 km/h again and the temperature rose to 475 °C such that the regeneration has started. The temperature profile of the aged filter resembled the CoO_x coated filter at the onset of the regeneration. Further regeneration decreased the temperature as well as the pressure drop to values closer to the mixed oxide coated filter.

4. Conclusions

In this study, onboard stability tests of a molten mixed oxide diesel soot oxidation catalyst were performed after being coated on a Cordierite DPF. The balance point temperatures of the onboard tests and peak temperatures of the loose contact laboratory reactor tests were similar confirming both the catalytic activity of the monolith coated catalysts and the validity of the laboratory tests conditions. The concentration profiles of the active materials monitored after use on the ceramic DPF indicated that the more mobile component (Pb) has migrated along the direction of flow during use and accumulated at the end of the filter. During the migration of this component, some eutectic regions on the filters were generated which were very active in soot oxidation. However, the stabilization of the molten metal oxide catalysts still remains as an issue after this work. The use of molten catalysts in DPFs will require alternative technological measures to avoid the escape of the molten phase by vaporization or by migration to the environment.

Acknowledgements

Chemical analyses of the catalysts were performed by the METU Chemical Engineering Department, Instrumental Analysis Group. SEM-EDX measurements were performed at the METU Metallurgical and Material Science and Engineering Department. V.E.G. kindly acknowledges the financial support from TOFAS during his MS studies.

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