

Preparation and Morphological Characterization of a Catalytic Soot Oxidation SiC Foam Filter

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The coating characteristics of Pb-Co mixed metal oxide soot oxidation catalysts over a SiC foam filter were studied. The coating was done via incipient wetness impregnation of a slurry with Pb/Co weight ratio = 2. The coating was accomplished by 3 consecutive impregnation-drying-calcination cycles. After each cycle surface structure and composition were monitored by scanning electron microscope (SEM). SEM analysis revealed that the surface composition of Pb was high on the high porosity region and surface composition of Co was high on the low porosity region inside the filter. These overlayers were tested for their soot oxidation ability by depositing paraffin soot from a candle flame, thermally oxidizing, and collecting SEM pictures before and after oxidation. SEM pictures after soot deposition/oxidation cycles revealed that high amounts of Pb were necessary for efficient removal of soot. However, Pb composition of the surface decreased due to the evaporative loss of Pb.

Key Words: Soot oxidation catalysts, SiC, Co, Pb, foam filter.

Introduction

Lean burn engines, particularly diesel engines, have been used for a long time in heavy-duty vehicles and for long-range transportation.¹ They are also becoming increasingly popular for passenger cars because of high efficiency and better fuel economy in comparison to gasoline engines.^{2,3} Combustion in the diesel engine results in the production of particulate matter (PM), comprising of mainly soot.^{4,5} Catalytic and non-catalytic diesel particulate filter (DPF) systems are extensively studied for the optimal solutions needed for the present and upcoming regulations of PM.⁶⁻⁸ Catalytic DPF systems provide a number of secondary advantages for the practical applications of the DPF system, including oxidation of hydrocarbons and CO slipping from the engine.⁹ In non-catalytic DPF devices, a trap and a regeneration system are needed, while catalytic filters are designed to self-regenerate.^{10,11} Catalysts oxidize unburned hydrocarbons and carbon monoxide with a gas-solid catalyzed reaction and oxidize soot particles with solid-solid catalyzed reactions.¹² Metal oxides having low melting points and eutectic mixtures are commonly used as a catalyst in the soot oxidation in order to create high surface mobility, and hence higher contact points. Nonetheless, the volatility of these types of catalysts probably explains why the stability of some of the reported catalysts was low.

In previous studies in our laboratory, it was shown that mixtures of Pb and Co oxides ensured low ignition temperatures and very fast rates of soot combustion as a result of the presence of a molten Pb phase. However, it was also shown that this mobility of Pb damaged the stability of the catalyst.^{13,14} In a previous study, Pb-Co mixed oxide was coated on the cordierite wall-flow type filter by using incipient wetness impregnation and the Pb:Co stoichiometry (w/w) ratio was 2:1.¹⁴ In the present study, a Pb-Co metal mixed oxide was coated on a SiC foam filter by using incipient wetness impregnation in 3 consecutive steps. A scanning electron microscope (SEM) was used to monitor the morphology of the Pb-Co mixed oxide coating while energy dispersive X-ray (EDX) analyses were performed to determine the local compositions. Furthermore, XRD analyses were performed to determine the crystal structure whenever appropriate. These analyses were carried out for 3 different regions in the filter. The effects of soot oxidation on the coating morphologies and catalyst stability were also monitored.

Experimental

Pb-Co mixed metal oxide was coated on a silicone carbide open cell foam filter. Prior to the coating, the filter samples were cleaned with a surfactant solution consisting of a mixture of ethyl alcohol, detergent, and distilled water in an ultrasonic bath for 20 min. Then the samples were dried and subsequently were etched in 1 M HCl solution. Finally the samples were washed in an ultrasonic bath for 20 min and dried.

Pb-Co metal mixed oxide catalysts were coated on the filter via impregnation. The slurry was prepared to have a Pb:Co stoichiometry (w/w) of 2:1 based on the optimum metal ratio determined in a previous study.¹⁴ CoO_x (Ege Ferro) was used for the source of cobalt oxide and $\text{PbAc} \cdot 3\text{H}_2\text{O}$ (Riedel De Haen) was used for the source of PbO_x . Elemental analysis of the cobalt oxide powder was done by atomic absorption spectrometry (Philips PU 9200X). The slurry was prepared by adding cobalt oxide powder to an aqueous solution containing an appropriate amount of $\text{PbAc} \cdot 3\text{H}_2\text{O}$. The slurry was continuously stirred during the coating. The coating was done by dipping the sample in the slurry at a rate of 40 cm/min, keeping it there for 20 min, and eventually removing it at a rate of 40 cm/min. During the whole process the slurry was stirred continuously to maintain a uniform composition. The samples were dried at 120 °C for 20 min and calcined at 300 °C for 2 h. Three samples were prepared by using the same procedure with different coating thicknesses. The sample coated once, twice and 3 times will be referred to as the first, second, and third piece, respectively. It must be noted here that before the second coating the slurry was put in a laboratory oven and kept there at 120 °C for 1 h until 100 mL of water had evaporated. In order to keep a uniform composition throughout the coating, lost water was compensated for before the second and third layer coatings. After each impregnation-drying-calcination cycle surface structural analyses were done by SEM (JEOL JSM 6400 equipped with an energy dispersive X-ray, EDX, Noran System 6) and X-ray diffraction (Ricaqu XRD with Cu target). For SEM and XRD analyses 3 different regions in the filter were selected: a low porosity (80 ppi (pores per inch square)) region outside the filter (first region), a low porosity (80 ppi) region inside the filter (second region), and a high porosity (10 ppi) region (third region), as shown in Figure 1.

Paraffin soot was deposited on the surface of these filters using a candle, followed by soot oxidation. Soot on the filter was oxidized in the oven at 400 °C for 1 h. These deposition and oxidation steps were repeated 2 more times. After each deposition and oxidation step one segment of the filter piece was cut and analyzed with SEM and XRD. In addition, elemental analyses of the local crystal structures were performed by EDX analysis.

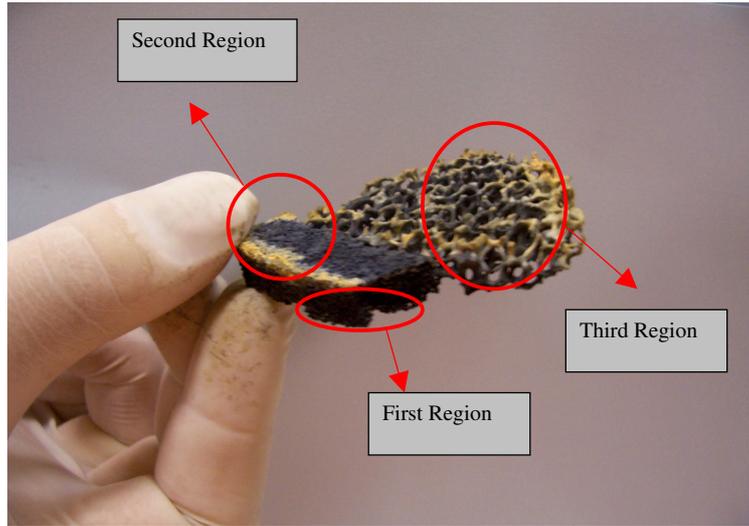


Figure 1. Sampling regions of the substrate filter.

Results and Discussion

XRD analysis of the bare filter revealed 2 distinct SiC phases and 1 SiO₂ phase. The elemental analysis of the cobalt oxide (CoO_x) powder by atomic absorption spectrometry (AAS) revealed trace amounts of Pb, Ca, Mg, Cr, Si, Ni, and Fe. The EDX analysis results of the coated samples presented in Table 1 indicated that the surface concentration of Pb is higher in the high porosity region and the surface concentration of Co is higher in the low porosity region inside the filter. The sampling zones are indicated in Figure 1.

Table 1. The chemical compositions of the coatings as determined from the EDX analysis sampled from different regions of the filter.

Sampling zone	Two layers of coating			Three layers of coating		
	1	2	3	1	2	3
Pb(wt%)	42.1	62.7	74.7	30.3	53.3	89.2
Co(wt%)	49.1	36.3	24.1	69.3	43.9	8.0
Ca(wt%)	-	-	1.2	-	2.0	1.8
Si(wt%)	7.3	1.0	-	0.4	0.8	1.0
Al(wt%)	1.3	-	-	-	-	-
Pb/Co weight ratio	0.9	1.7	3.1	0.4	1.2	11.1

SEM surface images of the 3 regions after the second and third layers of coating are shown in Figures 2 and 3. EDX analyses of the large crystals seen on the surface were observed to have close Pb/Co ratios with intended stoichiometry. It was also observed that after the second layer of coating large surface crystals were formed in the low porosity region outside the filter (2-2) and high porosity region of the filter (2-3), which were not observed in the 1 layer and 3 layer coated samples. Formation of larger crystals was attributed to the thermal treatment of the slurry prior to the second layer coating as described in the experimental part.

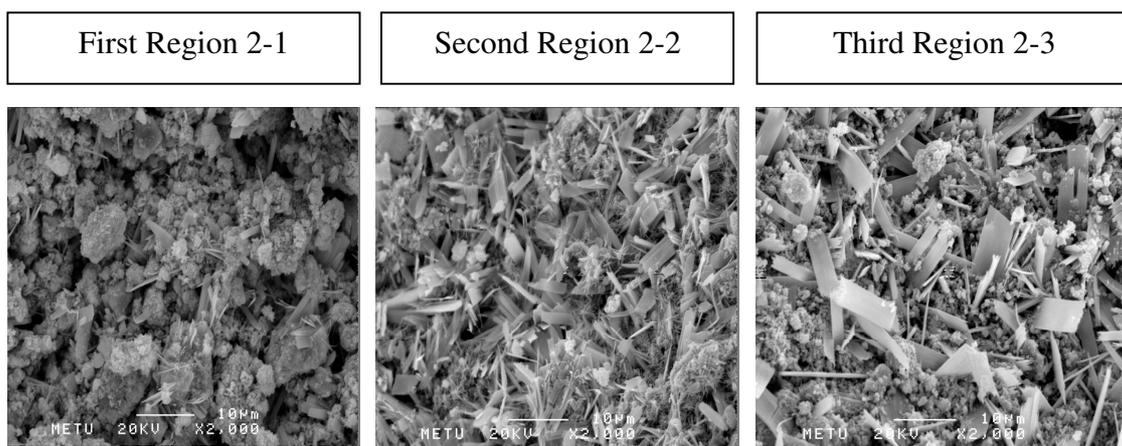


Figure 2. SEM images of different regions after second layer of coating.

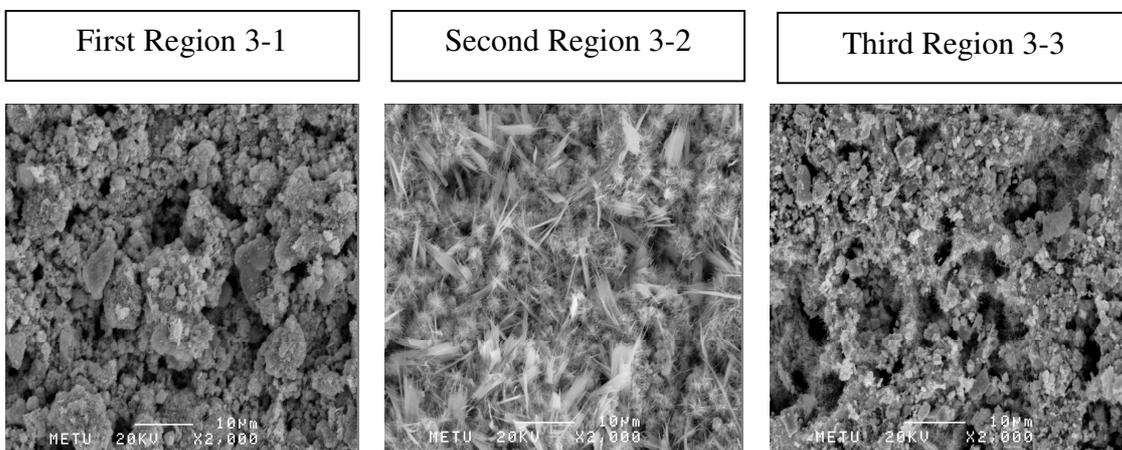


Figure 3. SEM images of different regions after the third layer of coating.

After each layer of coating, the phases of CoO_x and PbO_x on the surface were determined by XRD analysis for 3 different regions. XRD analysis indicated that 2 cobalt oxide phases were present in the form of CoCo_2O_4 and Co_3O_4 , and 2 lead oxide phases were present in the form of PbO with orthorhombic and tetragonal crystal structures. Furthermore, metallic lead (Pb) was also detected on the surface.

On the filter with 3 layers of coating, paraffin soot was deposited on the filter and the soot oxidation was performed in a laboratory oven at 400°C . The soot deposition-oxidation cycle was repeated 3 times. The morphology of the catalyst was monitored via SEM images. The EDX analysis results of the samples are presented in Table 2. Since the samples are taken from different regions of a heterogeneous sample, the absolute values are not comparable. However, it is clearly observed that over foam filters after 3 cycles of soot deposition-oxidation cycles Pb has disappeared through evaporative losses. SEM images (not shown) revealed that in the regions of high Pb concentration soot was rare, indicating the catalytic role of Pb . However, in the regions with large amounts of CoO_x the presence of soot was observable even after the oxidation cycle.

The morphology, chemical compositions, and the crystal structures of these catalysts before and after soot deposition-oxidation cycles are shown in Figure 4 a-d. It is visible from Figures 4-a and 4-d that there are regions in the filter where high crystallinity and whisker formation can be observed. The chemical compositions of these regions with different crystallinities were monitored via EDX in different zones (A and B) and are presented in Table 3. It is clear from Figure 4 and the elemental analysis presented in Table 3

that the whiskers belong to the Pb phases. This assignment is justified by the EDX analyses as well as the fact that the treatment temperatures (500 °C maximum) are not high enough to induce chemical or phase transformations in CoO_x phases.

Table 2. Surface compositions after the soot deposition and oxidation cycles. For reference, the compositions of the unused filter are also shown.

	Unused filter with 3 layers of coating	First cycle of soot deposition and oxidation		Second cycle of soot deposition and oxidation		Third cycle of soot deposition and oxidation	
		After soot deposition	After soot oxidation	After soot deposition	After soot oxidation	After soot deposition	After soot oxidation
Pb(wt%)	30.3	43.2	17.2	21.5	20.1	-	-
Co(wt%)	69.3	31.2	78.9	24.9	77.2	85.8	100.0
Si(wt%)	0.4	21.8	2.9	45.0	2.7	14.2	-

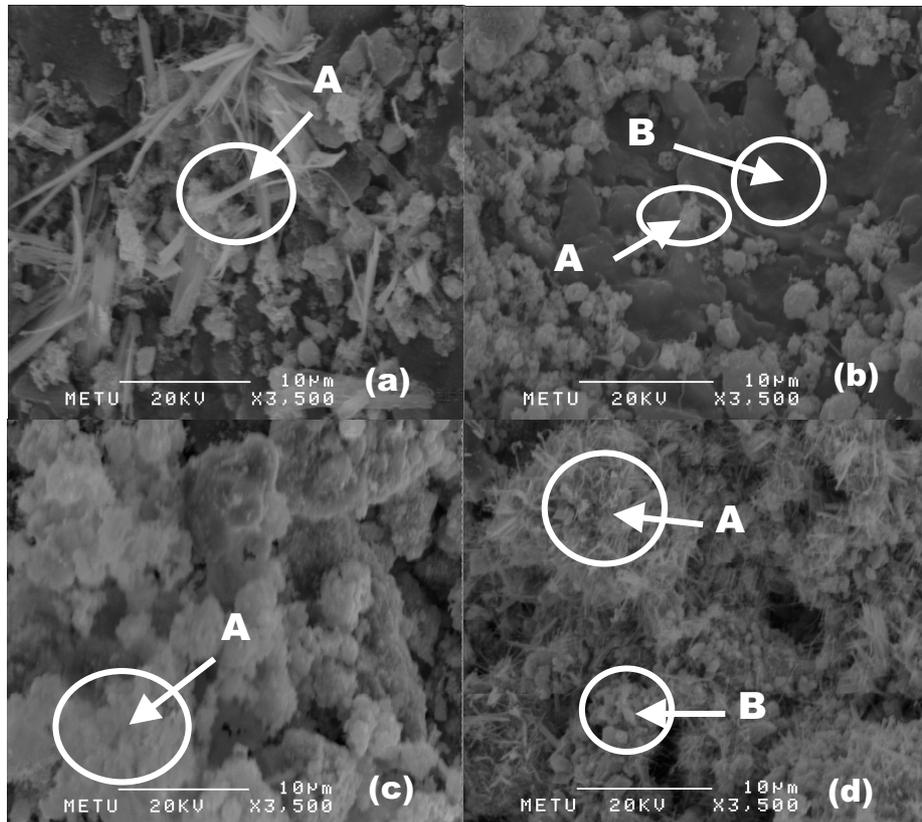


Figure 4. (a) High porosity region in the filter after third soot oxidation cycle, (b) Low porosity region inside the filter after second soot deposition, (c) Co rich zone in the low porosity region inside the filter after first soot oxidation, (d) Pb rich zone in the high porosity region after first soot oxidation.

Conclusions

A Pb-Co mixed oxide catalyst was successfully coated on SiC foam filters. It was observed that during preparation the oxides segregated to different regions of the filters: Pb preferred the high porosity region

while Co preferred the low porosity region in the filter. Pb rich zones were more active during the soot oxidation as monitored by the SEM images of the soot layers of Pb rich and Co rich zones. Phase analyses showed that cobalt oxide exists in the form of CoCo_2O_4 and Co_3O_4 . Pb is present in the form of metallic lead and PbO on the surface. High Co concentrations lead to cubic crystals and high Pb concentrations lead to tetragonal and orthorhombic crystals that are characteristic crystal structures detected by XRD. Furthermore, it was observed that after 3 cycles of soot deposition-oxidation almost all of the Pb deposited on the surface was lost.

Table 3. Elemental surface concentrations in the local regions shown in Figure 4-a, b, c, d.

	(a)		(b)		(c)	(d)	
	A	A	B	A	A	B	
Pb(wt%)	72.9			23.0	48.2	77.7	
Co(wt%)	14.9	86.2	-	74.9	51.9	22.3	
Si(wt%)	10.5	11.0	91.5	2.2			

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