



## Catalytic ceramic paper for the combustion of diesel soot

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### ABSTRACT

This work analyzes the application of a ceramic paper to the diesel soot combustion reaction in air. The catalytic paper is made of ceramic fibers, cerium oxide and potassium nitrate. The synthesis of this material is easy and fast, and provides a high-temperature resistant paper that can be readily adapted to different conformations and geometries. The presence of potassium and cerium as active ingredients confers high catalytic activity for the reaction studied under loose contact, showing a maximum combustion rate at 395 °C.

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### 1. Introduction

The major pollutants emitted by diesel engines are soot particles and nitrogen oxides, the combination of a filter with oxidation catalysts being the most widely studied after-treatment process to eliminate diesel soot particles [1]. Usually, commercial filters are made using ceramic or metallic materials [2–4], in the form of wall flow, metal fleece, and foams.

Another material that has been extensively used as particle filter is cellulose paper, which can be flexibly adapted to different conformations. In the case of diesel soot oxidation, the filter should resist the high temperatures of the exhaust, a requirement that cannot be met by cellulose fibers. However, it has been recently shown that the use of ceramic fibers along with cellulose ones and the application of papermaking techniques result in high-temperature resistant ceramic papers [5,6]. Either during or after the synthesis of the ceramic paper, a catalyst can be added; thus, a ceramic paper with catalytic properties is obtained.

In the last few years, the idea behind the so called “catalytic paper” has been to apply this paper for making structured catalysts for different reactions, for example methanol steam reforming [5–8] and the reduction of NO<sub>x</sub> in exhaust gases [9,10]. Recently, diesel soot oxidation in NO<sub>x</sub> catalytic traps has been proposed as an alternative to simultaneously eliminate both NO<sub>x</sub> and particles [11]. Thus, the ceramic catalytic paper could also be applied as a structured system for the simultaneous abatement of both diesel contaminants.

The purpose of this work is to explore the possibility of using catalytic papers to make efficient self-regenerating diesel soot filters. To this end, commercial ceramic fibers were used to make the ceramic paper. Cerium oxide and potassium nitrate were added as active ingredients to catalyze the diesel soot combustion reaction. The catalytic papers so obtained were characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA) and differential thermal analysis (DTA). Their catalytic behavior for diesel soot combustion in air was determined using TGA and DTA.

### 2. Experimental

#### 2.1. Synthesis of Catalytic Papers

The catalytic ceramic paper was prepared in two stages (Fig. 1): in the first stage, a ceramic paper loaded with cerium oxide was prepared; in the second stage, the final catalytic paper was obtained after the impregnation of potassium nitrate.

##### 2.1.1. Ceramic Paper Preparation

A papermaking technique with a dual polyelectrolyte retention system was used. Ceramic fibers composed of 48 wt.% Al<sub>2</sub>O<sub>3</sub> and 50 wt.% SiO<sub>2</sub>, with an average length of 659 μm (SD: 541 μm) and an average diameter of 6.3 μm (SD: 2.5 μm), were used. Cellulosic fibers correspond to bleached softwood kraft pulp.

Dry ceramic fibers (5 g) were added to a 500 ml solution volume (0.4 mEq/l) of PolyDADMAC (cationic polydiallyldimethylammonium chloride, molecular weight between 400,000 and 500,000 g mol<sup>-1</sup>, charge density 6.19 meq g<sup>-1</sup>, Aldrich) and NaCl (0.01 N) under agitation. Then, 1.5 g of CeO<sub>2</sub> and 2 g of calcium borate were incorporated, followed by 0.2 mEq/l of polyelectrolyte A-PAM

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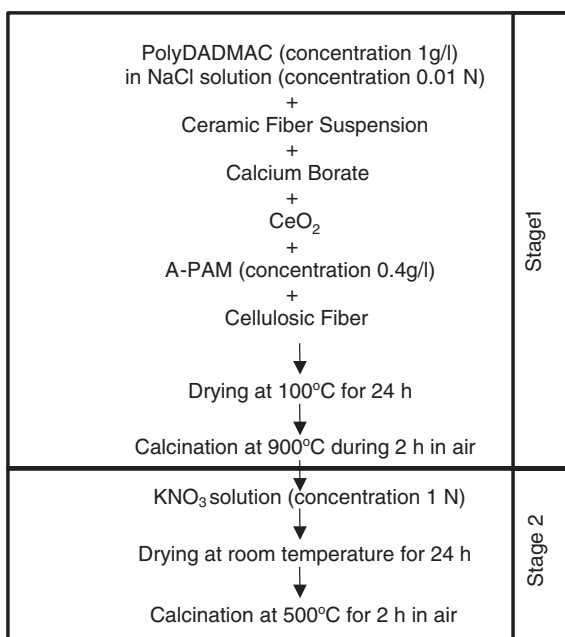


Fig. 1. Synthesis of the catalytic ceramic paper. Stages of the preparation procedure.

(anionic polyacrylamide, molecular weight between 10,000 and 100,000  $\text{g mol}^{-1}$ , charge density 2.74  $\text{meq g}^{-1}$ , Aquatec) and subsequently by 0.25 g of cellulosic fiber. With this suspension, a sheet was structured using the SCAN standard method but applying the double of the usual pressing pressure. The sheet (16.5 cm in diameter) was dried at 105 °C during 24 h and finally calcined in air for 2 h at 900 °C. This high temperature is needed to cause the fusion of the binder (calcium borate). The paper formed in this stage was called “ceramic paper”.

### 2.1.2. $\text{KNO}_3$ Impregnation

The addition of  $\text{KNO}_3$  to the ceramic paper was carried out by moistening a piece of the paper with a 1 M  $\text{KNO}_3$  solution until saturation. After that, the wet paper was dried at room temperature for one day, and finally, it was heated up to 500 °C at 0.5 °C/min and calcined at 500 °C for 2 h. The paper obtained in this stage was called “catalytic ceramic paper” and contained 6 wt.% of K and 11 wt.% of Ce.

## 2.2. Physicochemical and Morphological Characterizations

X-ray diffractograms were obtained with a Shimadzu XD-D1 instrument with a monochromator using Cu  $\text{K}\alpha$  radiation at a scan rate of 1°/min, from  $2\theta = 10$  to 80°. The pieces of about 2 cm × 2 cm were supported in a special sample holder designed for the XRD analysis. The software package of the equipment was used for the phase identification.

The thermal behavior of the ceramic papers was studied in a Mettler Toledo TGA/SDTA 851 instrument. The weight changes and the differential thermal process of the catalytic ceramic papers were analyzed from 25 to 900 °C with a heating rate of 10 °C/min in air flow (90 ml/min).

### 2.3. Diesel Soot Combustion Activity

The diesel soot was obtained by burning commercial diesel fuel (Repsol–YPF, Argentina) in a glass vessel. After being collected from the vessel walls, the diesel soot was dried in a stove at 120 °C for 24 h. More details about the obtention and characterization of diesel soot are reported elsewhere [12].

The activity of the solids for the diesel soot combustion reaction was studied by TGA in the same instrument and conditions as in the thermal studies described above. The diesel soot was homogeneously impregnated in the different samples using a suspension of 600 ppm of diesel soot in n-hexane. Usually, 10 mg of ceramic paper (or catalytic ceramic paper) + diesel soot mixtures were heated from 25 to 900 °C at 10 °C/min in an air flow of 90 ml/min. Results are presented in terms of the relative mass, defined as the weight at any temperature  $T$  divided by the initial weight,  $w^\circ$  (relative mass =  $w(T)/w^\circ$ ).

## 3. Results and Discussion

The method of preparation of the ceramic paper described in Section 2 is based on a procedure similar to that used in the production of conventional paper from cellulose fibers. In this case, the ceramic fibers and the catalyst particles are dispersed in the aqueous medium in which a binder should be added (calcium borate in our case) to give mechanical resistance to the final ceramic paper. After that, some amount of cellulose fibers is added in order to conform the paper matrix, and the standard paper manufacturing procedure is followed. The method requires the addition of a cationic polyelectrolyte followed by the addition of an anionic one in order to form solution complexes and a double layer over the fibers and particles which favor the formation of a fibrous layer.

Fig. 2 depicts the XRD patterns of the ceramic paper and the catalytic ceramic paper. In the former, the only signals observed are those corresponding to  $\text{CeO}_2$  (JCPDS-ICDD 34-394). For the catalytic ceramic paper two groups of signals appear; some of them belong to  $\text{CeO}_2$  and the others are due to the presence of  $\text{KNO}_3$  crystals (JCPDS-ICDD 5-377). In order to study the thermal stability of the catalytic ceramic paper, a piece of it was treated in air at 900 °C for 2 h. In this case, besides the  $\text{CeO}_2$  signals, a new phase,  $\text{KAISiO}_4$  (JCPDS-ICDD 11-579), was detected. It is convenient to remark that the commercial ceramic fibers used in this work are mainly composed of  $\text{SiO}_2$  and  $\text{Al}_2\text{O}_3$  (50 wt.%  $\text{SiO}_2$ , 48 wt.%  $\text{Al}_2\text{O}_3$  and 2 wt.% impurities), although these components do not exhibit peaks in the corresponding XRD diffraction patterns (not shown), which indicates that they are under the form of amorphous structures.

Figs. 3 and 4 show TGA and DTA results, respectively, obtained with the catalytic ceramic papers with and without diesel soot. The catalytic ceramic paper (Fig. 3, continuous line) exhibits a pronounced weight loss, which is in correspondence with an endothermic peak at

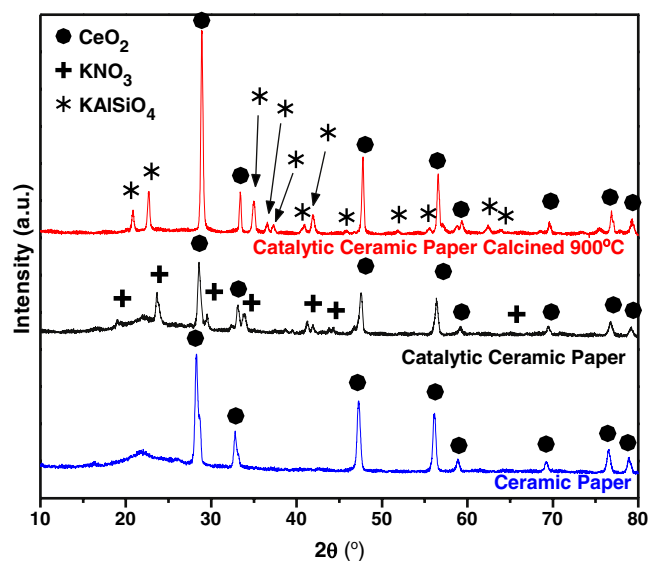


Fig. 2. Crystalline phases detected by XRD in the ceramic paper, the catalytic ceramic paper and the catalytic ceramic paper calcined at 900 °C.

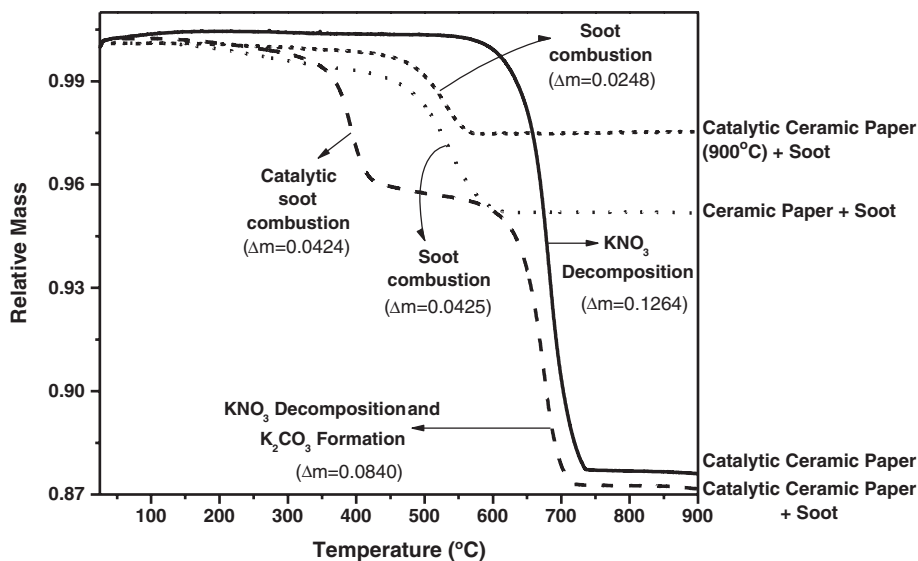


Fig. 3. TGA experiments. Experimental conditions: 90 ml/min of air and a heating rate of 10 °C/min.

ca. 675 °C (Fig. 4, DTA profile) and belongs to  $\text{KNO}_3$  decomposition into  $\text{NO}_2$  and  $\text{K}_2\text{O}$ , in agreement with reported results [13,14]. The TGA profile does not show the cellulose decomposition since the ceramic paper had been previously calcined at 900 °C and cellulose burns at temperatures close to 350 °C [15]. Fig. 4 also shows a small endothermic peak at ca. 330 °C, which corresponds to the melting of the alkaline nitrate (the  $\text{KNO}_3$  reported melting point is 338 °C, [16]), which is also present in the DTA obtained for the same catalyst mixed with diesel soot. The melting of the alkaline salt, which takes place just before the diesel soot combustion ignition, enhances the diesel soot-to-catalyst contact thus increasing the catalytic activity. After diesel soot addition, the catalytic ceramic paper impregnated with diesel soot exhibits a TGA profile with two marked weight losses: the first one produced by the catalytic combustion of diesel soot (395 °C) and the second one due to potassium nitrate decomposition (675 °C), as in the case of the catalytic paper without diesel soot. In correspondence, the DTA curve (Fig. 4) shows that the first peak is exothermic and the second one endothermic. The temperature of

maximum combustion rate is 395 °C, which is comparable to that of good catalytically active catalysts, taking into account the characteristics of the diesel soot-to-catalyst contact (loose contact). It is accepted that the impregnation carried out with a soot suspension in an organic solvent gives place to a loose soot-to-catalyst contact [17].

In the case of the ceramic paper impregnated with diesel soot (Fig. 3, dotted line), the TGA curve presents a weight loss between 500 °C and 600 °C (ca. 530 °C) associated with the diesel soot combustion exothermic process (Fig. 4). This range of temperature is in agreement with the one reported by Aboukaïs et al. for diesel soot combustion in  $\text{Al}_2\text{O}_3$  or  $\text{CeO}_2$  under loose contact conditions [18,19].

When the catalytic ceramic paper was calcined at 900 °C,  $\text{KNO}_3$  decomposed into  $\text{NO}_2$  and  $\text{K}_2\text{O}$ ;  $\text{K}_2\text{O}$  reacted with  $\text{Al}_2\text{O}_3$  and  $\text{SiO}_2$  from the ceramic fibers and formed  $\text{KAISiO}_4$  (see XRD patterns, Fig. 2). When the resulting catalytic ceramic paper calcined at 900 °C was impregnated with diesel soot, the TGA and DTA profiles were similar to those obtained with the ceramic paper (compare Figs. 3 and 4). That is, the calcination at 900 °C provokes the loss of the  $\text{KNO}_3$  active

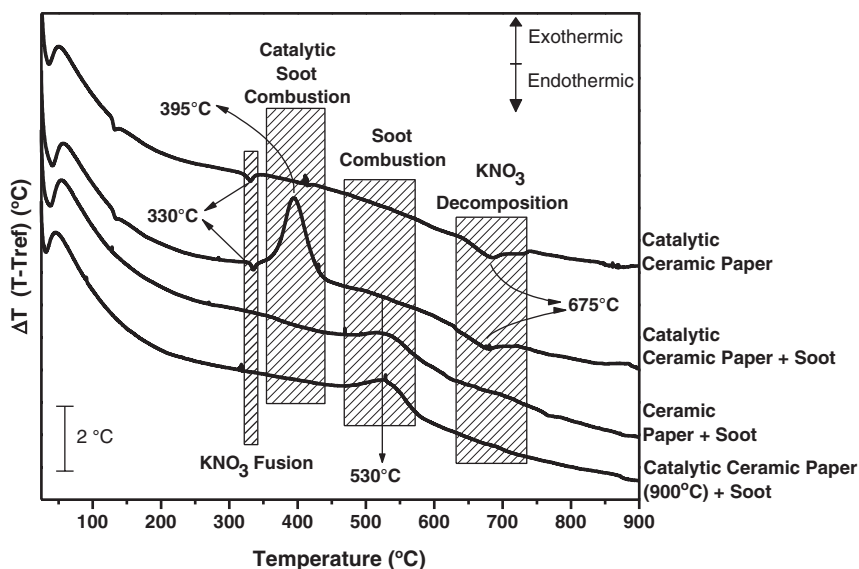


Fig. 4. DTA experiments. For experimental conditions see Fig. 3.

ingredient with the corresponding catalytic deactivation. Although this experiment was performed in order to study the thermal stability of the catalytic ceramic paper, it is not expected that the catalyst would work at this high temperature because typical diesel exhausts are close to 300–400 °C.

If we observe Fig. 3 in detail, it can be seen that the weight lost during the decomposition of potassium nitrate in the catalytic paper without diesel soot (Fig. 3, continuous line) is higher than the amount of nitrates decomposed when diesel soot is present (Fig. 3, dashed line, second step). This effect was reproducible in several experiments and could be ascribed to the formation of stable carbonates from the CO<sub>2</sub> released during the diesel soot combustion, as we observed in a previous work for potassium catalysts supported on lanthanum oxide [20]. That is, the weight loss observed in the TGA profile for the catalytic ceramic paper (Fig. 3) is  $\Delta m = 0.1264$  and that of the catalytic ceramic paper impregnated with diesel soot corresponding to the potassium nitrate decomposition is  $\Delta m = 0.0840$ . It should have been expected for both values to be the same. As said before, this apparent discordance could be associated with the simultaneous processes that occur in the case of the catalytic ceramic paper impregnated with diesel soot. Hüttinger and Mingos [21] found that the activation of KNO<sub>3</sub> starts by its decomposition ( $2\text{KNO}_3 \rightarrow \text{K}_2\text{O} + \text{O}_2 + \text{NO} + \text{NO}_2$ ). NO<sub>2</sub> would react with diesel soot to form CO<sub>2</sub> ( $\text{NO}_2 + \text{C} \rightarrow \text{CO}_2 + \frac{1}{2} \text{N}_2$ ), which in turn reacts with K<sub>2</sub>O to give K<sub>2</sub>CO<sub>3</sub>. The K<sub>2</sub>CO<sub>3</sub> melting point is 891 °C and only decomposes when the temperature is higher than the melting point [22], so that this carbonate is still present at the end of the TGA experiment and causes in part an increase in weight. Another phenomenon that could simultaneously take place is the interaction between NO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> and that of Ca with CO<sub>2</sub>. This complex reaction system is the origin of the apparent discrepancies found in the weight losses during the different experiments.

#### 4. Conclusions

The results show that the application of the catalytic paper concept is a promising alternative for making catalytic filters to be used in diesel contaminants abatement. The fibrous nature of the paper would allow modulating the porosity in order to improve the filtering capacity. The synthesis of the catalytic ceramic paper is easy, fast, and provides a material that can be simply adapted to different conformations and geometries. The presence of potassium and cerium

as active ingredients confers a high catalytic activity for the diesel soot combustion reaction under loose contact. Very high temperature treatments (900 °C) result in the formation of KAlSiO<sub>4</sub> and a deactivation of the catalyst, which is a drawback of this system that should be improved.

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