Catalysis Communications 72 (2015) 116–120

Contents lists available at ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short communication

Catalytic ceramic papers for diesel soot oxidation: A spray method for enhanced performance

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ARTICLE INFO

Article history:
Received 22 July 2015
Received in revised form 19 September 2015
Accepted 21 September 2015
Available online 25 September 2015

Keywords:
Diesel soot combustion
Aerosol spray drying
Catalytic ceramic paper
Exhaust catalyst
Cerium
Cobalt

ABSTRACT

A spray method is proposed to improve the catalytic properties of ceramic papers to be used as catalytic filters for removing diesel soot particles. Small particles of Ce and Co oxides, acting as active centers for the combustion of the soot retained by the filter, are efficiently and homogeneously deposited. On the contrary, the application of the conventional drip method results in bigger particles mainly agglomerated at the crossings between the fibers of the ceramic paper. As a result, catalytic papers prepared by the spray method exhibit much higher performance with soot combustion temperatures decreased by ~30 °C.

1. Introduction

The most adequate technology for the abatement of soot particles coming from diesel engines is the one that employs catalytic filters [1–4]. Nowadays, commercialized filters consist of SiC monoliths with active elements on them [5–8]. As an alternative, it was proposed to use ceramic papers as suitable materials to conform flexible structured catalysts for diesel filters [9–14]. Indeed, such papers are flexible, easy to handle and present suitable mechanical properties to resist assays from a test bench in which they were placed inside a metal housing, at the exhaust pipe outlet of a Corsa 1.7 diesel vehicle [9]. Optimal mechanical properties were obtained through the incorporation of a suspension of CeO_2 nanoparticles (10 or 20 wt.% CeO_2) during the papermaking process.

The passive regeneration of the filter implies the addition of catalytic components [15]. In this contribution, two different methods are used and compared in order to achieve the best distribution of the catalytic components (cerium and cobalt oxides) throughout the ceramic matrix: drip impregnation and spray deposition. The first method involves the impregnation by dripping a solution of precursor salts containing the desired catalytic components, followed by calcination. The second one is inspired by the aerosol process [16,17], which is currently emerging as a powerful tool for the preparation of advanced materials, especially catalysts [18–22]. The preparation is carried out in a dedicated experimental setup (Fig. 1), which consists of an aerosol generating system coupled with a tubular oven in which the formed droplets are dried rapidly. This dried aerosol is directly sprayed onto the ceramic paper disk.

The catalytic behavior was studied by means of TPO experiments in order to evaluate the feasibility of passive regeneration of the filters and physicochemical properties were evaluated by XRD and SEM.

2. Experimental

2.1. Ceramic paper preparation

The preparation method of the ceramic paper was based on a procedure similar to that used in the production of conventional paper from cellulose fibers and that is in detailed described elsewhere [9]. The ceramic fibers, 660 μm long (SiO_2–Al_2O_3) were dispersed in the aqueous medium in which a binder was added (10–20 wt.% of CeO_2 nanoparticles, Nyacol). Ribbon-shaped cellulose fibers, 3000 μm long, were also incorporated to enhance the retention of the ceramic fibers during the formation stage. The cationic polymer used was polyvinylamine (PVAm) (Luredur PR 8095) and the anionic polymer was anionic polyacrylamide (A-PAM).

A two-step method was employed for the preparation of catalytic ceramic papers. In the first step, following the papermaking technique,

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http://dx.doi.org/10.1016/j.catcom.2015.09.013
1566-7367/

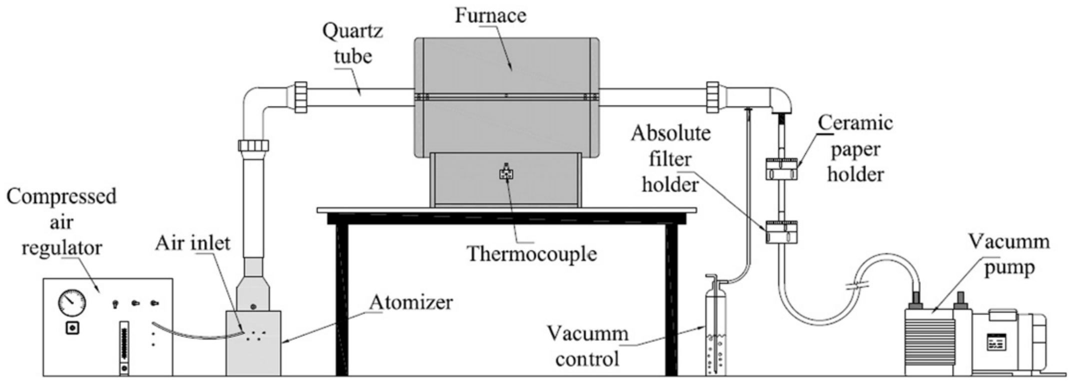

Fig. 1. Scheme of the spray deposition setup.

a sheet (16.5 cm in diameter) was formed and dried under controlled atmosphere (23 °C, 50% R.H.) for 24 h and finally calcined in air at 600 °C for 2 h. The second step corresponded to the deposition of the catalytic ingredients. Two series of catalysts were prepared, one following the conventional dripping method and the other using the spray technique.

2.2. Drip impregnation

The incorporation of the catalytic ingredients by drip impregnation was carried out using an equimolecular solution of $Ce(NO_3)_3$ and $Co(NO_3)_2$, which was prepared by dissolving the necessary amount of each precursor salt in the volume of water calculated to saturate the paper structure, so as to load 4 wt.% of $Ce(NO_3)_3 + Co(NO_3)_2$. The impregnated ceramic papers were then dried at room temperature overnight and calcined in a furnace at 600 °C for 2 h. The catalysts were denoted as 10Ce–Ce–Co–600–Imp and 20Ce–Ce–Co–600–Imp, where "10Ce" or "20Ce" indicate the wt.% CeO_2 binder used, "Ce-Co" the active components added, "600" the final calcination temperature and "Imp", the use of the drip impregnation method.

2.3. Spray deposition

In the second case, a mixed equimolecular solution of $Ce(NO_3)_3$ (0.622 g/l) and $Co(NO_3)_2$ (0.556 g/l) was placed in an atomizer (6-Jet 9306A atomizer from TSI) and sprayed with an air pressure of 30 psi (Fig. 1). The aerosol was dried by passing through a tubular furnace heated at 400 °C and the particles were directly sprayed onto the ceramic papers. Any excess particles exiting across the paper were retained by an absolute filter. The spraying time (6–8 h) were adjusted in order to load 4 wt.% $Ce(NO_3)_3 + Co(NO_3)_2$ on the ceramic paper disks. The sprayed ceramic papers were then calcined in a furnace at 600 °C for 2 h. The actual loading was verified by weighing. Catalytic papers are denoted as 10Ce–Ce–Co–600–Spray and 20Ce–Ce–Co–600–Spray.

2.4. Characterization

Crystalline phases were determined with a Shimadzu XD-D1instrument with monochromator using CuKα radiation at a scan rate of 2°/min, from $2\theta = 15°$ to 80°. The pieces of about 16 mm in diameter were supported in a special sample holder designed for the XRD analysis. The software package of the equipment was used for the phase identification from the X-ray diffractograms.

A SEM Jeol JSM-35C equipment was employed, operated at 20 kV acceleration voltage. Samples were glued to the sample holder with Ag painting and then coated with a thin layer of Au in order to improve the images.

2.5. Soot combustion

Soot particles were produced by burning a commercial diesel fuel (YPF, Argentina) in a glass vessel. After being collected from the vessel walls, the soot was dried in a stove at 120 °C for 24 h. Soot particles were dispersed in n-hexane using an ultrasonic bath in order to obtain a homogeneous suspension of 600 ppm of diesel soot in n-hexane. The incorporation of soot particles to the ceramic paper pieces (2 cm in diameter disks) was carried out by adding the suspension drop wise until saturation, and then drying at room temperature.

The catalytic activity of the ceramic papers for the soot combustion was studied by Temperature Programmed Oxidation (TPO). For this purpose, the structured samples + soot were heated at 5 °C/min from room temperature up to 600 °C in O_2 (18%) + NO (0.1%) diluted in He (total flow 20 ml/min) in a flow equipment designed for this purpose. We have chosen the oxygen concentration (18%) in order to compare our catalytic results with others previously published. The exhaust gases were analyzed with a Shimadzu GC-2014 chromatograph (with TCD detector).

In order to assess catalysts stability, two different experiments were carried out: 1) Thermal aging in air at 900 °C during two hours, and 2) several consecutive TPO cycles. In the latter, catalytic ceramic paper disks were recovered at the end of each TPO run and re-impregnated with soot before being tested again in TPO (from room temperature to 700 °C).

3. Result and discussion

SEM micrographs of the catalytic ceramic papers prepared using both preparation methods are shown in Fig. 2. Open structures are observed both for 10Ce–Ce–Co–600–Imp and 10Ce–Ce–Co–600–Spray. In order to analyze the penetration of Co and Ce introduced by drip impregnation and spray deposition methods through the thickness of the ceramic paper, SEM micrographs were obtained both on the top face (Fig. 2A and C) and also on a slice obtained by cutting the disk at the middle of its thickness (Fig. 2B and D). For both impregnation methods the amount of particles deposited both on the top face and in the bulk appear similar. It is interesting to note that catalytic particles formed in the spray process are retained inside the paper that is acting as a filter, which is the behavior expected during the operation in the tail pipe of a diesel exhaust.

In the case of the drip impregnation method Ce and Co oxides mainly appear concentrated in the form large chunks (>10 μm, see Table 1) on ceramic fibers crossings. On the contrary, when the spray method is employed (10Ce–Ce–Co–600 Spray), smaller catalytic particles (at least one order of magnitude smaller, see Table 1) appear well distributed throughout the ceramic matrix (Fig. 2C and D).