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Development of sepiolite/SiC porous catalytic filters for diesel soot abatement.

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Abstract

Honeycomb monoliths made up of 70 wt.% sepiolite and 30 wt.% SiC were prepared and macropores were generated in the honeycomb structure by introducing a temporary additive with the aim of obtaining an adequate porosity to use the structures prepared as diesel soot filters (DPF). CLARIMEX activated carbon was the most suitable among the additives studied.

In order to generate wall-flow type filters, it was also necessary to investigate suitable materials to alternatively plug the channels of the honeycomb monolith, finding that refractory mortar finely milled and mixed with water formed a paste easy to apply, which adhered firmly to the walls of the monolith being thermally and mechanically resistant.

The incorporation of Co and Ce as active phases was performed by successive impregnation followed by calcination at 600 °C. This system presented satisfactory results with respect to the maximum temperature of soot combustion rate, which is in the range of the diesel exhaust gases temperature (300 - 450 °C).

The wall-flow catalytic monoliths developed have similar characteristics to commercial diesel particulate filters in spite of having 70 wt. % of natural clay in its composition. The pore size remains to be further modulated in order to achieve a better permeation flow, similar to that of commercial filters, which could be tried out using larger particle size activated carbons.

Keywords: diesel particulate filter; wall-flow monolith; sepiolite and SiC; pore-generating agents.

1. Introduction

Emissions provoked by diesel engines, both in stationary and mobile installations, are a matter of great environmental concern. Particulate matter and NO_x are the main pollutants in diesel engine emissions. Diesel soot, constituted by very small particles carrying various suspected mutagenic hydrocarbons, can deeply penetrate into the lungs while NO_x compounds contribute to both acid rain and photochemical smog [1].

Strict regulations, such as the Euro 6 in Europe and EPA 2010 in USA, pose severe limitations in the amount of contaminants that can be emitted. Consequently, the automotive industry must invest big amounts of money and research efforts in order to meet the regulations [2-5]. As a matter of fact, last year, several newspapers worldwide reported the difficulties encountered by various car models equipped with diesel engine to pass standard tests for emission control. For this reason, great research efforts in developing more efficient catalytic processes to eliminate NO_x and diesel soot have been made during the last twenty years.

Existing technologies are highly sophisticated, and they usually consist of four units: a combustion catalyst, a NO_x trap, a particulate filter (PDF) and a catalytic reactor that selectively reduces NO_x to nitrogen using the SCR process with ammonia. Ammonia is provided by the decomposition of the urea stored in a tank [6-9].

The main objective of our research is to develop a more simple system, consisting of a ceramic filter impregnated with a combustion catalyst and a NO_x trap, thus promoting the reaction between NO_x and particles to eliminate both contaminants simultaneously.

In a previous work [10], mesoporous monoliths with tailored macroporosity were obtained by extrusion, using sepiolite clay and different pore generating agents. Cobalt, barium and potassium were incorporated as active phases during the kneading of the dough or by impregnation of the structured material to give the monoliths the capacity to burn soot catalytically under the conditions of diesel engine exhausts. However, we concluded that important properties like an adequate mechanical resistance and porosity should be improved. The former is obviously necessary due to the demanding conditions in a real engine exhaust, and the latter in order to efficiently retain the small soot particles without exerting an excessive pressure drop.

Sepiolite is a natural hydrated magnesium silicate clay (with chemical composition $\text{Si}_{12}\text{Mg}_8\text{O}_{30}(\text{OH})_4(\text{H}_2\text{O})_4 \cdot 8\text{H}_2\text{O}$). The advantages of natural sepiolite as a support are micro-porosity and high mesoporosity, which provide the material with a high surface area ($300 \text{ m}^2 \cdot \text{g}^{-1}$), and excellent rheological properties of pastes produced using water as lubricant, which allow that extrusion in various shapes occurs. The surface area is reduced after calcination at high temperature, but an important proportion of the mesopores is maintained, thus permitting the impregnation and dispersion of active phases [11]. Indeed, sepiolite is a valuable clay for industrial applications owing to its fibrous structure, high porosity, high specific surface area, good adsorptive, rheological and catalytic properties [12,13].

In this work, we report the preparation, characterization and catalytic evaluation of filters made by extrusion of Sepiolite/SiC mixtures together with different pore generating agents. SiC is incorporated in the monoliths in order to improve both mechanical resistance and porosity. Catalytic ingredients were also added to decrease the temperature of soot combustion during filter regeneration: Co, K, Ba and Ce were used in line with previous works in which we studied active formulations for the reaction mentioned [14,15]. The filters were prepared by alternatively plugging the end of the monolith channels, thus forcing the gases to pass through the porous walls of the channels. In this way, the system acts as a wall-flow diesel particulate filter trap. Different materials were tested in order to close the ends of the channels in a convenient way.

Several studies were performed in order to assess the characteristics of the filters, i.e. mechanical resistance with a dynamometer, compression tests, Mercury Intrusion Porosimetry (MIP) and permeation capacity. The morphology of the monoliths was looked into using both optical and SEM microscopy. Finally, the temperatures necessary for the regeneration of the filters were determined by means of Temperature-Programmed Oxidation (TPO) experiments including NO (1000 ppm) in the gaseous feed.

2. Experimental

2.1 Honeycomb monoliths

Different supports and additives, such as pore generating agents (PGA) listed in Table 1, were mixed to prepare dough for manual extrusion with a syringe. Water was slowly incorporated until an extrudable paste was formed. An aliquot was extracted to determine the humidity

percentage and the rest was introduced into the syringe and extruded. Part of the "noodles" obtained was further kneaded to form discs. Both types of structures were then calcined at 850°C or 1000°C for 2 h. The discs were employed to determine the shrinkage after calcination. The extrudable combinations of support and temporary additives that led to calcined monoliths exhibiting a low degree of shrinkage, good mechanical resistance, high pore volume, pore size distribution with maximum between 10-20 μm [16,17] and a high specific surface area were selected to be extruded in the extrusion machine. Honeycomb monoliths with different geometry, size, wall thickness and number of channels were obtained by changing the type of nozzle.

2.2. Development of wall-flow catalytic filters

2.2.1. Addition of the catalyst to the honeycomb monoliths

The incorporation of catalytically active components to the supporting monoliths was carried out by successive impregnation according to results obtained in previous studies [18,19]. Individual precursor solutions of $\text{Co}(\text{NO}_3)_2$, $\text{Ba}(\text{Ac})_2$, KNO_3 and $\text{Ce}(\text{NO}_3)_3$ were prepared to achieve this aim. The concentrations of individual solutions were calculated considering the volume that would completely fill the monoliths pores (determined by MIP) and a desired loading: 12 wt.% Co, 16 wt.% Ba, 7 wt.% K and/or 38 wt.% Ce (values referred to the final monolith mass). The calcined supporting monoliths were immersed into the corresponding solution for 5 min in an ultrasonic bath (40 KHz). Then, they were blown with air, dried at room temperature overnight and calcined at 600°C for 2 h after each impregnation step. The active phase order in the sample name is representative of the impregnation order.

2.2.2 Alternative plugging of honeycomb monolith channel ends

The materials tested to block the ends of the channels, either alone or combined with additives, and using water or liquid glass as solvent, are listed in Table 2. The mixture was applied with a spatula to every other channel of the monoliths (1 g each 64 channels endings); after being forged for 2 days, the monoliths were calcined at 600°C for 2 h.

2.3. Physical characterization

2.3.1. Mechanical resistance

Crush strength was determined with a Chatillon dynamometer. Radial crush strength of noodles (σ) was calculated as the ratio between the maximum force applied before breaking (F) and the length of the noodle ($L = 0.5\text{--}1\text{ cm}$) when the force was applied through a mobile plate.

In the case of honeycomb monoliths, crush strength values were determined by changing the mobile plate for a broach. Axial crush strength (P) was calculated as the ratio between the maximum force applied before breaking (F) and the broach area ($7.85 \times 10^{-7} \text{ m}^2$).

2.3.2. Compression tests

Compression tests were performed in a universal testing machine, Shimadzu DSS-10T model. A Shimadzu N° 22771 cell, with a load capacity of 500 kg, was used. It was calibrated with loads of 10.0 kg in the range of 0.0 kg up to 50.0 kg under the same test conditions. Compression tests were carried out at a constant speed of 0.5 mm/min at a temperature of $24.0 \pm 0.5^\circ\text{C}$, and a relative humidity of $70 \pm 5\%$.

2.3.3. Mercury intrusion porosimetry (MIP)

A CE Instruments Pascal 140/240 apparatus was used to determine pore volume and neck size distributions over the range of 7.5 nm to 300 μm . The Washburn Equation [20] was used to analyze the pressure/volume data assuming a cylindrical non-intersecting pore model, taking the mercury contact angle and surface tension as 141° and 484 mN.m^{-1} , respectively [21]. Samples were dried overnight at 150°C prior to measurement to ensure that they were free from any loosely bound adsorbed species.

2.3.4. Morphological characterization: scanning electron microscopy (SEM)

A JEOL JSM-35C SEM was employed at 20 kV acceleration voltage. The samples were glued to the sample holder with Ag painting and then coated with a thin layer of Au in order to improve conductivity.

2.3.5. Permeation

A specific system was designed and constructed to determine the permeation of porous monoliths [14]. The permeation system contained a cylindrical stainless steel reservoir where the monolith was loaded. The flange and bolts built up the closure and a thermoplastic polymer sealed the joint since measurements were recorded at room temperature.

The permeability of wall-flow filters, both without and with different loads of soot, was determined by measuring the outlet air flow when modifying the inlet pressure. Experimental data were fitted using the model proposed by Payri et al. [22], based on a lumped parameter model for pressure drop calculation in honeycomb wall-flow monoliths proposed by Konstandopoulos [23]. This model evaluates the pressure drop produced when a gas enters into the channels of a monolith and passes through its porous walls. It also considers pressure drop due to the compression of the gas at the channel inlet and its expansion at the channel outlet. Taking into account these considerations, the lumped parameter model equation is:

$$\Delta P_{DPF} = a.Q + b.Q^2$$

Where ΔP_{DPF} (bar) is the pressure drop between the inlet and the outlet of the wall flow filter, Q (ml.s^{-1}) is the air volume flow measured at the outlet of the permeation equipment, and a and b are parameters that take into account pressure changes due to both the passage of the gas flow through the porous walls and changes in the flow section of channels, respectively.

2.3.6. Optical microscopy

Images were obtained with a Leica Zoom 2000 Stereomicroscope, coupled with a digital camera for image capture.

2.4. Catalytic activity tests: Temperature-programmed oxidation (TPO)

Catalytic activity for soot combustion was studied by temperature-programmed oxidation (TPO). For this purpose, soot particles were obtained by burning commercial diesel fuel (YPF, Argentina) in a glass vessel. The soot collected from the vessel walls was dried at 120 °C for 24 h. Catalytic monoliths were immersed into a homogeneous suspension of soot in n-hexane (10000 ppm) and then dried at room temperature which guaranteed realistic soot to catalyst contact, as

studied previously [24]. The soot-containing samples were heated at $5^{\circ}\text{C}\cdot\text{min}^{-1}$ from room temperature up to 600°C in O_2 (18%) + NO (0.1 %) with He as balance (total flow $20\text{ ml}\cdot\text{min}^{-1}$) in a flow equipment designed for this purpose. The exhaust gases were analyzed in a Shimadzu GC-2014 chromatograph with a TCD detector.

3. Results and discussion

A systematic study was carried out in order to optimize the support compositions for the preparation of ceramic honeycomb monoliths. In order to attain this aim, manual syringe extrusion was employed firstly in order to select the best raw materials in terms of rheological and mechanical properties, which were then used to manufacture honeycomb monoliths by mechanical extrusion.

3.1. Support optimization

3.1.1. Sepiolite

A complete list of additive compositions tested for the extrusion of sepiolite with a manual syringe is included in the Supplementary Information section (Table S1). The best performing compositions in terms of rheological properties of the dough and mechanical properties of sepiolite extrudates are summarized in Table 3. In addition, we made a list of the crush strength values obtained after calcination at 850 or 1000°C , which completely removed the additives and transformed the supports into thermally and chemically stable structures.

The main textural properties of samples listed in Table 3 are compared in Figure 1. Pore size distribution curves of all the noodle-like samples obtained with biopolymers such as pore generating agent exhibit a bimodal distribution, with mesoporosity associated to sepiolite and macroporosity generated by the removal of the organic additive (Figure 1.A). As an exception, carboxymethylcellulose (CMC) seems to have filled the micro porous of the silicate; probably, after calcination, unburnt residues of CMC obstruct the access to the microporous structure. Both wheat and rice starch (WS or RS) generated too small macropores, between $1\text{-}2\text{ }\mu\text{m}$ in diameter, whereas sawdust (S) or carboxymethylcellulose (CMC) generated larger pores, but lower cumulative pore volumes. Although the sizes of the macropores generated with CMC are in the

range needed to efficiently filter soot, 10-20 μm , their amount is low which led us to further study different types of activated carbon (Figure 1.B), in accordance with previous results [10]. Bimodal distribution is observed again. Carbon type C (C), Asbury (As) and Clarimex (Cl) generated macropores of similar size, ca. 4 μm , whereas F5 led to slightly bigger pores, ca. 9 μm in diameter. In addition, the pore volume produced with F5 activated carbon is twice as much or more than the volume produced with the rest of the PGA tested. In agreement with Tuler et al. [10] this indicated that sepiolite is used as support material, the best selected PGA found among all listed in Table 1, is F5 carbon. Other materials, apart from sepiolite, were tested as supports to enhance porosity and mechanical resistance.

3.1.2. Silicon Carbide (SiC)

Two different types of commercial SiC powders were studied as starting material, being one black (SiCb) and the other green (SiCg). They show not only different purity, but also differences in particle size, being the larger ones those corresponding to the black SiC. A complete list of the additive compositions tested for extrusion of SiC with a manual syringe is included as Supplementary Information (Table S2). The best performing compositions in terms of rheological properties of the dough and mechanical properties of the SiC extrudates are summarized in Table 4 together with the crushing strength values obtained after calcination at 850 or 1000°C. SiC extrusion from commercial powders requires the use of a binder to form a paste since it has an inert and large particle size and it is not possible to extrude it by adding water only. Among the different additives tested, CMC resulted in the most compatible binder for SiC, and it also had the function of generating pores after calcination (Table S2).

The textural properties of the SiC samples listed in Table 4 were determined by MIP. All SiC extrudates showed monomodal pore size distributions (Figure 2) irrespective of the starting SiC powder or additives used. When black SiC was used, the pore size was between 60-70 μm , being these large pores detrimental to filtration efficiency. In the case of green SiC, the maximum in pore size distribution profile appeared at 23 μm . Although this value can be acceptable if soot aggregate sizes are considered, the cumulative pore volume is low, making it difficult to impregnate active phases and to decrease soot filtration capacity.

Mixtures of SiC + sepiolite were studied considering that smaller amounts of larger pores were obtained using SiC as support whereas larger amounts of smaller pores were obtained in the case of sepiolite (Figure 2).

3.1.3. Sepiolite + SiC mixtures

Different mixtures of sepiolite + SiC (containing 30, 50 or 70 wt.% SiC black, green or a mixture thereof) combined with different proportions of activated carbons were extruded with the syringe to optimize support composition (Table S3, Supplementary Information). SiCb led to more resistant noodles than SiCg, and the addition of high amounts of sepiolite further improved both rheology and mechanical resistance. Thus, the mixture 30 wt.% SiCb + 70 wt.% Sep was chosen as the support to evaluate the best AC type and the proportion to be added to the mixture.

Table 5 summarizes the mechanical properties of the best noodle-like samples extruded, calcined at different temperatures. As expected, the higher the PGA content, the more the porosity. However, the maximum percentage of PGA that could be incorporated was limited to 30-40 wt.% (depending on the PGA used) by mechanical resistance. In order to produce resistant extrudates, 1000°C was selected as calcination temperature.

Figure 3 shows the cumulative pore volume and pore size distribution of the noodles obtained with the compositions indicated in Table 5. All samples exhibited a bimodal pore size distribution (as seen for pure sepiolite noodles, Figure 1), with mesopores associated with the sepiolite and high macropores of ca. 4-8 μm in diameter in all cases, higher than those obtained using the bare sepiolite and smaller than those obtained using only SiC. The macropores sizes are very close to the optimum range (10-20 μm) being the mechanical properties satisfactory, which led us to select Sep (70)SiCb (30) as the best support composition to prepare honeycomb monoliths.

Among the activated carbons tested, Norit and Clarimex led to mixed supports that exhibited the largest pore sizes and the highest pore volumes, meanwhile the mixture F5:Cl (30) gave supports the lowest cumulative pore volume, so this last mixture was discarded as PGA. In spite of exhibiting the highest cumulative pore volume and a suitable macropore size, Norit activated carbon produced the most fragile supports (0.8 kg.cm⁻¹). Besides, this AC is commercially available only as pellets, whose hardness makes it very difficult to mill to obtain the significant amounts needed for the extruder machine. Thus, Norit AC was discarded as well, being Clarimex, Asbury and F5 the type of carbons selected for extrusion tests in the mechanical extruder.

3.2. Honeycomb monoliths extrusion

Once composition and calcination temperature were optimized to obtain extrudates with a low degree of shrinkage, good mechanical resistance, high pore volume, pore size distribution with a maximum between 10-20 μm and high specific surface area, the preparation procedure was scaled up to prepare, by mechanical extrusion, honeycomb monoliths with the selected composition. This was a mixture of 70 wt.% sepiolite and 30 wt.% SiC black as supporting material and 40 wt.% of Clarimex, Asbury or F5 activated carbons as temporary additives. As a general trend, both pore volume and mean pore size decreased when the extruder machine was used instead of the syringe (compare Figures 3 and 4). Although the reduction in the cumulative pore volume was negligible (from 0.8 to 0.7 mL.g^{-1}), the mean size of pores significantly decreased (from 4-8 to 3-4 μm). This could be associated both to the better homogeneity of the dough obtained with the mechanical mixer and to the higher pressure applied to the extruder machine. Probably, the inter-particle spacing is diminished and the PGA agglomerates are smaller and consequently, pores generated after calcination are smaller too.

F5 or Asbury carbons led to similar textural properties, whereas Clarimex carbon produced monoliths with the highest mean pore size (4 μm) and the highest pore volume (0.72 mL.g^{-1}), despite having a lower mechanical strength (69 kg.cm^2) compared to the others (Sep (70)SiCb (30)F5 (40) = 138 kg.cm^2 and Sep (70)SiCb (30)As (40) = 132 kg.cm^2). Therefore, the Sep (70)SiCb (30)Cl (40) monolith was selected to further characterize its morphology by SEM, impregnate the catalytic components, test the activity and alternatively plug the channel ends so as to obtain particulate filters, then checking their permeation properties.

The higher mechanical resistance of monoliths containing SiC allowed us to decrease the wall thickness of prepared monoliths from 1 mm to 0.47 mm, the last denoted as TW (thin wall monoliths). Figure 5 shows photographs obtained by optical microscopy in which the dimensions of the channels and the wall thickness of thin wall monoliths can be appreciated.

3.3. Catalytic monoliths

Catalytic monoliths were obtained by successive impregnation of active components onto the optimized honeycomb support. The catalytic formulations incorporated to the monoliths were chosen according to previous results [10].

3.3.1. Morphology of the structured catalysts

Figure 6 shows the morphology of the bare Sep (70)SiCb (30)Cl (40) honeycomb monolith calcined at 1000°C and the catalytic monoliths obtained after the incorporation of Co,Ba,K or Co,Ce as active phases and calcination at 600°C.

A high macroporosity is observed for Sep (70)SiCb (30)Cl (40) structured support, with numerous macropores higher than 10 μm , in spite of MIP results that indicated a mean pore size ca. 4 μm . These wide open pores are beneficial to the filtrating function. A closer view shows a high interconnectivity of the macropores, which is also desirable in order to diminish pressure drop.

After the incorporation of catalytic components, the pore size slightly decreased, and either Co,Ba,K or Co,Ce appeared as irregular agglomerated (ca. 1-5 μm) homogeneously distributed all over the structured support. They covered both the external and internal pore surfaces, as indicated by the thicker wall of the pores, which increased from 0.5-1 μm to 2-3 μm .

3.3.2. Catalytic activity for soot combustion: TPO

Figure 7 shows the temperature-programmed oxidation profiles (18% O_2 + 0.1% NO) of the catalytic monoliths containing either Co,Ba,K or Co,Ce when feeding. The appearance of only one peak indicates that the soot is homogeneously distributed on the catalytic surface, which was achieved through the incorporation of soot into the structured catalysts from the suspension in n-hexane. This method of soot deposition was previously studied in our group [24] and it is the correct option to reproduce the working conditions in a diesel exhaust filter. Both active phase combinations, based on cobalt as the catalytic component for soot oxidation, provided the support with good activity considering the temperatures of Diesel engine exhausts (300 - 450 °C). The maximum soot combustion rate occurred at 417 °C for Co,Ce and at 454 °C for Co,Ba,K. In the case of the Co,Ce-containing monolith, the catalytic activity is intrinsically ascribed to the presence of the transition metal whereas cerium acts as oxygen storage element, and thus, provides surface atomic oxygen for soot combustion. The Co,Ba,K-containing monolith exhibited a TPO profile shifted to higher temperatures, despite the fact that the cobalt content within its formulation is the same. In this sample, barium is added to trap NO_x at low temperatures and release it at high temperatures, helping to burn soot, and the role of potassium is to enhance the catalyst-to-soot

contact. The lower activity of the latter indicates that potassium + barium can be replaced by cerium in the catalytic formulation, hence avoiding the use of potassium, which can be lost at high temperatures in the presence of water [25], and thus reducing the temperature required for the filter regeneration by combustion.

3.4. Wall-flow catalytic filters

By alternatively sealing the monolithic channels ends, they result in one being open and the other closed, so that a gas flow is forced to pass through the porous walls. Thus, the plugged monolith can act as a particulate filter, or even a catalytically regenerable filter if the active phase is present, thus improving NO_x trapping.

3.4.1. Channel endings sealing

The sealing material must be impermeable and should exhibit good adhesion to the walls of the monolith, low shrinkage coefficients as well as high mechanical and thermal resistance after calcination. To this end, we tested several materials and we qualitatively evaluated those factors as low, medium or high, on the basis of a visual observation of the sealed channels after calcination. Among the compositions tested (listed in Table 2), those that produced the best sealing after forge and calcination at 600 °C are discussed and shown in Figure 8. The refractory metal sealant produced very good adhesion and resistance, but the difference in contraction coefficients caused the breaking of the walls of the monolith after calcination (Figure 8A). In the case of quartz wool with liquid glass, the adhesion was also good, but the bubbles formed after calcination weakened the sealing increasing the probability of cracks formation (Figure 8B). Finally, Weber refractory mortar produced the best sealing after milling and sifting the material and mixing it with water so as to obtain dough with the adequate consistency to be applied. After calcination, the sealing so formed exhibited good adhesion and high strength, whereas shrinkage was negligible, as shown in Figure 8C. Therefore, this material was the most suitable for channel

ends sealing and hence it was used to develop wall-flow filters, i.e. honeycomb monoliths with their ends alternatively blocked.

Also, Figure 8D shows a honeycomb monolith with thin walls, Figure 8E shows the same monolith impregnated with Co, Ba, K and Figure 8F displays the monolith impregnated with Co and Ce.

3.4.2. Permeation

Figure 9 shows the permeation curves of wall-flow filters composed of bare sepiolite (Sep F5 (50)), bare SiCb (SiCb CMC (40)), or mixtures of sepiolite + SiC. The experimental values are well fitted with the Payri equation. The porous monolith composed by SiCb is the most permeable one, which is associated to its higher pore size, and that composed by bare sepiolite is the less permeable filter. It must be taken into account that higher pores favour permeation; however filtration efficiency diminished. The addition of 30 wt.% SiCb to sepiolite reduced the pressure drop with both F5 or Clarimex carbons as PGA (Sep(70)-SiCb(30)-F5(40) and Sep(70)-SiCb(30)-Cl(40)). However, the permeation was really improved when decreasing the thickness of the filter walls from 1.0 to 0.47 mm (Sep(70)-SiCb(30)-Cl(40)TW, TW referring to thin walls) since the wall thickness is an important parameter that affects the square coefficient "b" of Payri's equation.

In order to study the effect of the addition of the catalyst to the thin wall filter on its permeation capacity, ΔP vs. Q curves were evaluated both for the system containing Co,Ba,K and Co,Ce. The inset in Figure 9 shows the permeation measurements with catalytic wall-flow filters, i.e., Co,Ba,K/Sep(70)-SiCb(30)-Cl(40)TW and Co,Ce/Sep(70)-SiCb(30)-Cl(40)TW, respectively. The permeation curve for the bare support, Sep(70)-SiCb(30)-Cl(40)TW, is also included in the inset for comparison. Although the active phases were preferentially deposited inside the support pores increasing pore walls, as shown in Fig. 6, their addition did not significantly affect permeability.

Soot was added to the wall-flow filters to study its influence on the permeation properties (not shown). The pressure drop slightly increased in all samples, but not significantly. This highlights the importance of permeation in this type of wall-flow filters since it could determine the pressure drop of the filter when functioning in the diesel vehicle.

3.5 Comparison of developed wall-flow filters and commercial ones

In order to compare geometrical, mechanical and textural characteristics of the developed wall-flow filters, a similar commercial SiC device was chosen. Table 6 lists characteristics of both a commercial wall flow SiC filter and those prepared (Sep(70)-SiCb(30)Cl(40)TW, SiCb-CMC (25)TW). The commercial SiC DPF has a mean pore size within the defined optimal range for efficient filtration (11 μm) whereas SiC-CMC(25)TW and Sep(70)-SiC(30)-Cl(40)TW have higher and smaller pore sizes, respectively. However, porosity and maximum soot loading are higher, which represent lower pressure drop and higher filter capacity. On the other hand, mechanical strength of the filter with the mixed support is reduced due to the introduction of 70% of sepiolite to the SiC structure, which makes it weaker.

4. Conclusions

Honeycomb monoliths made of a mixed support, made up of 70 wt.% of natural, abundant and economic clay and silicon carbide were prepared. With a temporary additive, macropores are generated. The larger the particle or agglomerate additive particles, the larger the pores obtained. Among the PGA studied, Clarimex activated carbon was the most suitable for this mixture of support, being it able to further improve porosity and pore size using larger particles.

For wall-flow type filters, it was necessary to research materials needed to alternately plug the channels of the honeycomb monolith. The results indicate that refractory mortar finely milled and mixed with water forms a paste easy to apply. After two days of forging and further calcination at 600°C for 2 h, it formed an impermeable seal, well adhered to the walls of the monolith and thermally and mechanically resistant.

The incorporation of active phases to this structured support was also studied. In a previous work [10], it was concluded that successive impregnation with further calcination at 600°C for 2 h after each impregnation is the best method to obtain catalytic filters. Here the Co,Ce system presented satisfactory results with respect to the maximum temperature of soot combustion rate, which is in the range of the diesel exhaust gases temperature (300 - 450°C).

Permeation measurements showed that although the performance of commercial monoliths was not achieved, the wall-flow catalytic monoliths developed have very similar characteristics to commercial diesel particulate filters, in spite of having 70 wt.% of natural clay in its composition. The pore size remains to be further modulated in order to achieve the performance of the commercial filter, which could be tried out using larger particle size activated carbons, which would improve permeability.

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Figure legends

Figure 1. Cumulative pore volume (continuous line) and pore size distribution (dashed line) of sepiolite noodles manufactured using different additives: (A) biopolymers, (B) activated carbons. The number in brackets is the additive concentration expressed as wt.% of the sepiolite mass (see Table 3).

Figure 2. Textural properties of SiC noodles determined by MIP using different additives. The number in brackets is the additive concentration expressed as wt.% of the sepiolite mass (see Table 4).

Figure 3. MIP results of Sep (70)SiCb (30) noodles with different additives calcined at 1000 °C. The number in brackets is the additive concentration expressed as wt.% of the sepiolite mass (see Table 5).

Figure 4. MIP results of honeycomb monoliths made from sepiolite and SiC support (Sep (70)SiC (30)) with different additives, calcined at 1000 °C. The number in brackets is the additive concentration expressed as wt.% of the sepiolite mass.

Figure 5. Optical microscope photograph of thin-walled honeycomb monolith for the measurement of cell sizes and wall thickness.

Figure 6. SEM micrographs of Sep (70)SiC (30) honeycomb monoliths. Effect of the incorporation of active phases and closer view of pores.

Figure 7. TPO profiles for diesel soot combustion of catalytic honeycomb monoliths with different active phases: Co,Ba,K and Co,Ce. The temperature of the maximum burning rate is indicated.

Figure 8. (A-C) Images of sepiolite honeycomb monoliths with alternatively plugged endings used for the sealing: (A) refractory sealant for metals, (B) quartz wool with liquid glass and (C) refractory mortar. (D) Photographs of thin walled Sep(70)-SiCb(30)-Cl(40)TW honeycomb monoliths. (E) Co,Ba,K/Sep(70)-SiCb(30)Cl(40)TW and (F) Co,Ce/Sep(70)-SiCb(30)-Cl (40).

Figure 9. Permeation curves of the different honeycomb monoliths, compared with SiC and commercial cordierite ones. Inset: (-♦-) Sep(70) SiC (30) Cl (40)TW, (-●-) Co,Ba,K/Sep (70) SiC (30) Cl (40)TW, (-▲-) Co,Ce/Sep (70) SiC (30) Cl (40)TW.

Table 1. Nomenclature of raw materials used as supports and additives.

Nomenclature	Raw material
Support	
Sep	Sepiolite Pansil 100
SiCb	Silicon carbide F180 - black
SiCg	Silicon carbide F360 - green
Temporal additive	
Biopolymer	
CMC	Carboxymethylcellulose
HC	Hydroxymethylcellulose
MC	Methylcellulose
WS	Wheat starch
RS	Rice starch
S	Sawdust
Activated Carbon	
F5	Chemviron F5 type
C	Chemviron C type
Cl	Clarimex 0.61 CAE
As	Asbury 5565
Nor	Norit RST4 (milled pellets)

Table 2. Materials tested as sealants and qualitative characteristics of the sealing after forging and calcination.

Seal		Mechanical resistance	Thermal resistance	Shrinkage
Material	Solvent/Additive			
Liquid glass	-	Low	Low	Low
Sepiolite	Water	Low	High	Medium
	Liquid glass	Low	Low	High
	10 wt.% CMC + water	High	Low	High
	10 wt.% CMC + liquid glass	Medium	Low	High
	10 wt.% polyvinyl alcohol + water	Medium	Low	Medium
Quartz wool	Liquid glass	High	High	Low
Metal refractory sealant (Nural 29 Pattex®)	Water	High	High	High
	Liquid glass	High	Low	High
Refractory mortar (Beissier®)	Water	Medium	Low	Medium
	Liquid glass	High	High	Medium
	50 wt.% liquid glass + water	High	High	Medium
	10 wt.% sepiolite + 50 wt.% liquid glass + water	Medium	Medium	High
Refractory mortar (Weber®)	Water	High	High	Low

Table 3. Mechanical properties of sepiolite noodles extruded by the syringe technique.

Nomenclature	Additive type	Additive (wt.%)	Calc. temp. (°C)	Crushing strength (kg.cm ⁻¹)
Activated Carbon				
Sep-F5(50)	F5	50	1000	3.5
Sep-As(50)	As	50	1000	4.6
Sep-Cl(50)	Cl	50	1000	2.7
Sep-C(70)	C	70	850	>1
Biopolymers				
Sep-WS(100)	WS	100	850	>4
Sep-RS(100)	RS	100	850	>1
Sep-S(20)	S	20	850	>1
Sep-CMC(100)	CMC	100	850	>1

Table 4. Mechanical properties of SiC noodles using different additives.

Nomenclature	Support	Additive type	Additive (wt.%)	Calc. temp. (°C)	Crushing strength (kg.cm ⁻¹)
SiCb-F5(15)	SiCb	F5	15	1000	2.6
SiCg-CMC(25)	SiCg	CMC	25	850	>1
SiCb-CMC(25)	SiCb	CMC	25	850	>1
SiCb-CMC:F5(40)	SiCb	CMC:F5 (63:37)*	40	1000	2.6

* Relationship between PGA (wt. %).

Table 5. Mechanical resistance of noodles based on Sep(70)-SiC(30) calcined at different temperatures.

Nomenclature	Additive type	Additive (wt.%)	Calc. temp. (°C)	Crushing strength (kg.cm ⁻¹)
Sep(70)-SiCb(30)-F5(40)	F5	40	850	0.6
			1000	1.2
Sep(70)-SiCb(30)-As(40)	As	40	1000	2.0
Sep(70)-SiCb(30)-F5:Cl(30)	F5:Cl(50:50)*	30	1000	2.0
Sep(70)-SiCb(30)-Nor(30)	Nor	30	850	0.4
			1000	0.8
Sep(70)-SiCb(30)-Cl(40)	Cl	40	850	0.9
			1000	1.7

* PGA Ratio (wt. %).

Table 6. Technical specifications of commercial SiC DPF and properties of the developed wall-flow monoliths.

	Commercial SiC*	Sep (70)-SiC (30)-CI (40)TW	SiC-CMC (25) TW
Cell density	200 cpsi	140 cpsi	140 cpsi
Cell size	1.2 mm	1.7 mm	1.7 mm
Wall thickness	0.37 mm	0.47 mm	0.47 mm
Geometric segment surface area (GSA)	1.9 1/mm	1.44 1/mm	1.44 1/mm
Open frontal area	22.4 %	32 %	32 %
Mean pore size diameter	11 μ m	4 μ m	60 μ m
Porosity	48 %	66 %	57 %
Soot load limit	8-10 g/L	9-12 g/L	10-12 g/L
Compressive strength	15 Mpa	5 Mpa	5 Mpa

* Clean Diesel Ceramic (CDC) emission technology.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5.

Figure 6.

Figure 7.

Figure 8.

Figure 9.

Research Highlights

Wall-flow monoliths made up of 70 wt.% sepiolite and 30 wt.% SiC were prepared.

The porosity of the filters was tuned by the addition of pore generating agents.

Cobalt, barium, potassium and/or cerium were impregnated to develop catalytic activity.

Different materials were used to alternatively plug the channel ends to generate filters.

The thickness of the filter walls was varied so as to obtain good permeation properties.