



Catalytic filters for the simultaneous removal of soot and NO_x: Influence of the alumina precursor on monolith washcoating and catalytic activity

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ABSTRACT

Different highly dispersible boehmites were used as alumina precursors in the preparation of washcoating suspensions for the preparation of catalytic filters containing Cu or Co together with K as the active phase. Catalysts were characterized by means of SEM microscopy and N₂ adsorption, in order to determine their morphological and textural properties. Their activity in the simultaneous removal of soot and NO was assayed in a fixed-bed laboratory installation. Morphology of the deposited layer was found to strongly depend on the type of precursor used in the preparation of the washcoating suspension. Textural properties varied as well when employing the different precursors. In fact, the textural properties of the catalytic filters determined their activity, concretely towards NO reduction. Co-containing catalysts were found to be more active in general than Cu-loaded ones, particularly towards the elimination of NO_x. The catalysts prepared were able to selectively reduce NO at temperatures between 475 and 575 °C, by means of a simultaneous elimination mechanism taking place in the presence of the carbon material. Soot oxidation was found to be complete in most cases, and almost totally selective towards CO₂.

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1. Introduction

The increasing concern on atmospheric pollution derived from road transportation has led to the introduction of newer and each time more stringent regulation over the past decades. *Vis-à-vis* gasoline spark ignited engines, diesel engines operate under *lean* conditions, contributing to better fuel economy and lower CO₂ emissions, whereas controlled combustion temperature results in lower gaseous CO and HCs concentrations in the exhaust [1]. Therefore, and due also to their excellent durability, the demand for light-duty diesel vehicles has increased notably in the last years, this trend being expected to continue in the near term future [2]. The design of the combustion process in diesel engines does, however, result in higher emission of particulate matter, i.e. dry soot. Engine modifications, such as *common rail* technology, the introduction of four valves per cylinder and *exhaust gas recirculation* (ERG) cooling technology, have helped to lower the emission of particulates and other pollutants in diesel engines conforming the previously existing legislative demand. Still, there is always a trade-off between the reduction of particulate matter emission and nitrogen oxides (NO_x) control. Thus, the use of after-treatment technologies is required, and each time more efficient technologies

are being hunted in order to meet the upcoming emission standards [3].

Under typical operating conditions of diesel engines, three-way catalysts are not efficient in reducing NO_x [4,5]. Procedures such as selective catalytic reduction (SCR) [6,7] and NO_x storage-reduction (NSR) [8] allow the removal of nitrogen oxides from automobile exhausts under excess oxygen, and have been extensively studied in the last years. However, SCR systems need the presence of a reducing agent, normally urea, and its corresponding storage and feed units, entailing serious drawbacks to its implantation in light-duty vehicles, where space limitations are stricter and fuel economy is above all sought. NSR catalytic systems still suffer from serious problems such as low catalytic activity, narrow temperature window of operation and deactivation in the presence of other components in the exhaust [9].

It is widely known that NO₂ is highly reactive with soot, oxidizing it around 250 °C, typical of diesel engine exhausts during normal driving cycles [10,11]. However, NO₂ concentrations in exhaust are normally low (5–15% of total NO_x), and not sufficient to provide high soot oxidation rates [12]. The “continuously regenerating-trap” (CRT) technology utilizes a Pt-supported catalysts upstream the particulate filter, allowing partial conversion of NO to NO₂, which subsequently reacts with the soot retained in the filter [13]. Attempts have been made in the last years to substitute this two-stage catalytic system by a single device [14], which incorporates the catalyst on the surface of a filtering material [15]. However, in the presence of noble metal-based catalytic systems, only

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Table 1

Features of the four different highly dispersible aluminas employed as precursors.

	Disperal(D)	Disperal 20(D20)	Disperal 40(D40)	Disperal 60(D60)
d_{50} (μm)	25	30	50	50
S_{BET} (m^2/g)	180	150	100	95
Dispersed p.s. (nm)	80	150	300	350

Note: d_{50} refers to mean boehmite particle size, S_{BET} accounts for the BET surface area of the boehmites, while *dispersed particle size* indicates the mean size of the aggregates in the sols obtained using each precursor. All the data provided by Sasol GmbH.

partial reduction of NO_2 to NO was claimed to occur, with barely small amounts of NO_x totally converted to N_2 [16,17]. On the other hand, some other studies report successful NO_x conversion to N_2 in the presence of BaAl_2O_4 [18], CuFe_2O_4 [19], K–Fe [20], K–Cu and K–Co [21], La–Na–Cu–O [22], La–K–Cu–V–O [23] perovskites or Co–Al [24] mixed oxide catalysts, at intermediate temperatures from 350 to 600 °C. These studies show that simultaneous removal of both contaminants yielding CO_2 and N_2 as main products is possible, under certain reaction conditions and in the presence of an adequate catalytic system, normally containing transition metal oxides. In fact, in previous works [25,26] we reported high activity and selectivity towards N_2 and CO_2 for several alumina supported catalytic systems containing Cu, Co and V together with K as alkali promoter, also when supported in a conformed material such as cordierite monoliths, in view of their practical application for the catalytic filtering of diesel exhausts.

In the present paper we present a series of Me (Cu,Co)–K/ Al_2O_3 cordierite monolith-supported catalysts, prepared using four types of highly dispersible boehmites as precursors. Monolith coating, deposited layer properties and catalytic activity in the simultaneous removal of soot and NO_x , have been evaluated as a function of the different precursors used in their preparation.

2. Materials and methods

2.1. Preparation of the catalytic filters

Cylindrically shaped (1 cm diameter, 3 cm length) cordierite honeycomb monoliths ($2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$, Corning, 400 cpsi) were selected as conformed support for the preparation of the catalytic filters. Alumina suspensions were prepared by sol–gel synthesis, using as precursors four types of highly dispersible boehmites: Disperal, Disperal 20, Disperal 40 and Disperal 60, all of them supplied by Sasol GmbH. Highly dispersible boehmites have been widely used as catalyst supports [27,28], as well as in the synthesis of washcoating suspensions [29,30] or as primers [31], for the preparation of structured catalytic systems with similar applications. The particular features of each of these alumina precursors, mean powder particle size, d_{50} , surface area, S_{BET} , and dispersed particle size, according to the data provided by the manufacturer, are shown in Table 1. Either Cu and Co were added to the dispersions as the catalytically active metals, in the form of their corresponding nitrates $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (99% pure, Panreac) and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (98% pure, Panreac), together with K (KNO_3 ; 99% pure, Panreac) as the alkali promoter. Concentrated nitric acid (65 wt.%, Panreac) was added as peptizing agent. Different suspensions were prepared varying the alumina load and using different $\text{HNO}_3/\text{Al}_2\text{O}_3$ ratio, for a fixed Me to K mass ratio 5:10 with respect to the corresponding Al_2O_3 load, as shown in Table 2. Mixtures were stirred for 24 h. After this time, their pH (Crison GLP 21+ pHmeter) and viscosity (Brookfield DV-E viscosimeter) were determined. pH measurements were repeated after 4 days of ageing to determine its value after stabilization. Prior to their impregnation, cordierite monoliths were submitted to oxidation in concentrated HNO_3 for approximately 5 min. Coating was performed by means of forced circulation of the corresponding dispersion through the channels of the cordierite

monoliths, with the help of a peristaltic pump (Masterflex, Cole Palmer). After 30 min circulation time, the coated monoliths were dried in a rotatory oven at 60 °C during 24 h, and subsequently subjected to calcination at 450 °C for 4 h. Although the relatively low calcination temperature may result in the presence of residual nitrates in the catalysts, temperature programmed decomposition under Ar flow, heating up 300 mg of powder catalyst from 250 to 650 °C at 5 K/min, and following NO, N_2O and NO_2 evolution by mass spectrometry (Balzers 422) evidenced that, in the worst case, only 2.2% of the total K content in the catalyst remains in the form of KNO_3 after calcination.

2.2. Textural and morphological characterization of the catalytic filters

The prepared catalytic filters were characterized by means of scanning electron microscopy (SEM, Hitachi S-3400 N coupled with EDX analysis, Röntec XFlash), N_2 adsorption at -196°C (Micromeritics ASAP 2020), applying BET method for the calculation of sample's surface area, BJH and t -plot methods for the calculation of meso and micropore volume, respectively. The adhesion of the washcoat was evaluated by immersing the catalytic filters in a glass vessel containing n-heptane and submitting them to ultrasonic agitation in an ultrasonic bath (Medi II Pselecta), during three consecutive periods of 30 min. Weight loss after each agitation period was calculated and registered.

2.3. Activity measurements

Prior to the determination of the activity of the prepared catalysts, soot filtration was simulated by means of incorporating a model carbon compound. For this purpose, a carbon black (Elftex 430, Cabot, S_{BET} : 80 m^2/g , primary particle mean size: 27 nm) was selected, due to its identical behaviour upon thermogravimetric oxidation in air, in comparison to laboratory-produced diesel soot, as previously reported for other similar carbon blacks [32]. It is well known that real soot is a complex carbon material, whose features and reactivity depend on combustion conditions and fuel type [16,33,34]. The presence of the soluble organic fraction (SOF) in soot may contribute to increased reactivity of this material in comparison to carbon blacks [35,36]. Thus, the use of a carbon black as model compound in this work must be viewed as a conservative experimental approach to the catalytic combustion of real diesel soot. Each coated monolith was introduced for 1 min into a continuously stirred dispersion of 0.2 g of carbon black in 100 mL of n-pentane, removed and dried at 65 °C during 1 h. Weighting the filter before and after this process allows the determination of the amount of carbon black loaded in each case, which was about 10–20 mg in any case, corresponding to approximately 20 wt.% load with respect to the mass of catalytic material deposited on the surface of the monolith. As a result of this procedure for soot loading, “loose” contact between soot and catalyst can be considered as more representative in this case, according to the concepts of “loose” and “tight” contacts defined by Neeft et al. [37–39].

The catalytic activity of the filters in the simultaneous removal of soot and nitrogen oxides was tested by means of dynamic

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