

Cesium as Alkali Promoter in Me-Cs (Me = Cu, Co, Fe)/ Al₂O₃ Structured Catalysts for the Simultaneous Removal of Soot and NO_x

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ABSTRACT

Structured catalysts for the simultaneous removal of soot and nitrogen oxides were prepared by means of coating cordierite monoliths with alumina-based suspensions containing Cu, Co or Fe and Cs as the catalytically active phase. Textural and chemical properties of the coated monoliths were determined by means of N₂-physisorption, SEM and temperature programmed reduction. Their activity in the simultaneous removal of soot and NO_x was assayed in a lab-scale installation, using a carbon black as diesel surrogate. Catalysts containing Cs exhibited significant activity in deNO_x, however soot oxidation activity is poorly enhanced probably due to the low NO₂ evolution, pointing to a different NO_x adsorption mechanism in the present case, in comparison to previous observations on analogous K and Ba containing catalysts.

Keywords: Exhaust Gas Cleaning; NO_x Selective Reduction; Soot Oxidation; Cesium; Washcoating; Structured Catalysts

1. Introduction

In the last years, diesel vehicles have become leaders in the automobile market due to their excellent durability. This trend is expected to continue in the near-term future. In spite of the fact that diesel engines emit lower amounts of CO₂ and others pollutants, they are important sources for the emission of particulate matter *i.e.* soot [1]. Moreover, under typical operating conditions of diesel engines, *i.e.* lean-mixtures, three-way catalysts are not efficient in reducing NO_x [2].

The increasing concern about the environmental effects of these contaminants has led to the introduction of a newer and each time more stringent regulation [3]. The previously legislative demands have been achieved by means of implementing engine modifications, such as common rail technology, the introduction of four valves per cylinder and exhaust gas recirculation (ERG) cooling technology. Still, there is always a trade-off between the reduction of particulate matter emission and nitrogen oxides control. Thus, in order to meet the upcoming emission standards the use of after-treatment technologies is strictly required.

In order to reduce the concentration of NO_x from auto-

mobile exhausts under excess oxygen, procedures such as selective catalytic reduction (SCR) [4,5] and NO_x storage-reduction (NSR) have been previously considered. However, both alternatives suffer from serious difficulties in order to reach its effective implantation. SCR systems need the presence of a reducing agent, normally urea, and its corresponding storage and feed units, entailing serious drawbacks to its application 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.

The use of a catalyst in combination with particle filter is one of the most promising after-treatment techniques to reduce soot emission. An oxidation catalyst decreases the soot ignition temperature assisting the filter regeneration. NO₂ is a powerful soot oxidant, however NO₂ concentration in exhaust are normally low (5% - 15% of total NO_x) [6]. The “continuously regenerating trap” (CRT) technology utilizes a Pt-supported catalyst upstream the particulate filter, allowing partial conversion

of NO to NO₂, which subsequently reacts with the soot retained in the filter [7-10]. Attempts have been made to achieve the total reduction of NO₂ to N₂ simultaneously to soot oxidation. When using noble metal-based catalytic systems, only partial reduction of NO₂ to NO was reached, with small amounts of NO_x totally converted to N₂. On the other hand, some other studies report successful NO_x conversion to N₂ [11-16]. In previous works we reported high activity and selectivity towards N₂ and CO₂ for several alumina supported catalytic systems containing Cu, Co and V together with K as alkali promoter [17]. In general, in such catalytic systems the alkali promoter, mainly K, is thought to bring substantial benefits for soot oxidation, due to the formation of low melting point compounds, which improve soot-catalyst contact [14,18,19]. The major drawback of using K is its low stability, due to the relatively low melting point of its oxide compound, which is responsible for the short durability of the catalyst. Besides K, Cs based catalysts pose an option, which has been recently studied as an alternative for soot oxidation [19-22].

The aim of this work is to prepare and study Al₂O₃-supported Cu, Co or Fe systems, in combination with Cs as alkali promoter, with the aim of evaluating its activity in the simultaneous removal of soot and NO_x.

2. Experimental

2.1. Catalysts Preparation and Characterization

Cylindrical shaped cordierite monoliths (2MgO·2Al₂O₃·5SiO₂, Corning, 400 cpsi, 1 × 2.5 cm), were coated using different suspensions prepared by sol-gel synthesis, using a highly dispersible boehmite (Disperal, Sasol GmbH). Such highly dispersible aluminas have been previously employed as supports [23], in the synthesis of washcoating suspensions [24] or as primers [25], in the preparation of catalysts with similar applications. Cu, Co and Fe were added to the alumina suspensions (Cu(NO₃)₂·3H₂O, Co(NO₃)₂·6H₂O or Fe(NO₃)₃·9H₂O) together with Cs (CsNO₃) as alkaline promoter. Metal to promoter mass ratio was 5:15, for an alumina load of 5% wt., and HNO₃/Al₂O₃ ratio of 0.1. Mixtures were stirred for 24 hr; measuring viscosity and pH, after 4 days ageing time. Coating was performed by forced circulation of the suspensions through the channels of the monoliths, with the help of a peristaltic pump. After 30 minutes circulation time, monoliths were dried in a rotating oven at 60°C during 24 hours, and subsequently calcined at 450°C for 4 hours. **Table 1** presents a list of the different catalysts prepared, their labeling, coating suspensions and their viscosity and pH.

Physico-chemical characterization of the prepared catalysts was performed by means of scanning electron microscopy (SEM, Hitachi S-3400 N), and N₂ adsorption at

−196°C (Micromeritics ASAP 2020), applying BET method for the determination of surface area, BJH and t-plot methods for the calculation of meso and micropore volume. Catalyst stability, *i.e.* in terms of loss of alkaline and alkaline-earth promoter, was evaluated by means of intensive calcination of the catalyst at 800°C for 5 hours.

2.2. Activity Tests

Soot filtration was simulated by means of the incorporation of a carbon black (Elftex 430, Cabot, S_{BET}: 80 m²/g, primary particle mean size: 27 nm), selected due to its identical behavior upon thermo gravimetric oxidation in air, *vis-à-vis* laboratory-produced diesel soot. Still, the use of a carbon black can be considered as a conservative experimental approach, since the presence of soluble organic fraction (SOF) in real soot contributes to increased reactivity [26]. Each catalyst was introduced for 1 min into a continuously stirred dispersion of 0.2 g of carbon black in 100 mL n-pentane, and then dried at 65°C during 1 hour. Weighting the catalysts before and after allows the determination of the amount of carbon black loaded, which corresponded to approx. 20% wt. with respect to the mass of catalytic material deposited on the surface of the monolith.

The activity of the prepared catalysts in the simultaneous removal of soot and NO_x was assayed in a lab-scale fixed bed installation. A reactant gas containing 500 ppmv NO and 5% O₂ in Ar was flowed at 50 mL/min through a catalyst (1 × 2.5 cm). Experiments were performed at temperatures between 250°C and 650°C, heating rate of 5°C/min. Concentrations of the different compounds were analyzed by means of mass spectrometry (Balzers 422) and gas chromatography (Varian Micro GC CP 4900). NO conversion, X_{NO} , and X_{NO_x} were calculated from the molar concentrations: $X_{NO} = m_{NO} / m_{NO}^i$. Carbon black conversion, X_{CB} , was calculated using the initial amount of carbon black and the molar concentrations of CO and CO₂:

$X_{CB} = (m_{CO_2} + m_{CO}) / m_{CB}^i$. CO and CO₂ concentrations were determined by means of GC. NO, NO₂ and N₂ concentrations were calculated from the data registered by the MS, taking into account the possible contributions of the rest of the components to their corresponding principal m/z values of 30, 46 and 28. N₂O formation was assessed by comparison of concentration of CO₂ measured by GC and concentration obtained from m/z 44 in MS.

3. Results and Discussion

3.1. Catalysts Characterization

As previously discussed elsewhere [27,28], viscosity and pH of the suspensions, see **Table 1**, depend upon their composition. In this case, the use of Co results in less

viscous suspensions. In all cases suspensions show stabilization pH values lower than the one corresponding to alumina isoelectric point [around 3 - 4], pointing to incomplete H^+ consumption. In general, the use of Cs as promoter results in a somehow more complicated gelation process, yielding suspensions of lower viscosity and pH with respect to previous observations using K and Ba [29]. This fact can be ascribed to its higher ionic size in comparison to K and Ba [30]. In spite of the differences among the properties of these suspensions, coating of the cordierite monoliths results in similar amounts of catalytic material loaded, 10% weight on average, see **Table 1**. Uniform coating was observed in all cases; see **Figure 1** which presents SEM images acquired for FeK, FeBa and FeCs catalysts. **Table 1** shows as well average layer thickness measured by means of SEM inspection of the cross section of the coated monoliths, see as well **Figures 1(d)-(f)**.

Table 2 shows the results obtained in the textural characterization of the catalysts by means of N_2 adsorption. The catalysts exhibit surface areas, S_{BET} , between 8.8 and

$10.1 \text{ m}^2/\text{g}$, higher than in the originally macro-porous cordierite, pointing to pore filling upon coating. In fact, pore volume corresponds mostly to mesopores, with values ranging from 0.017 to $0.021 \text{ cm}^3/\text{g}$, and average pore sizes from 7.0 to 7.6 nm .

3.2. Catalytic Activity

Figure 2 shows the results obtained in the simultaneous removal experiments for FeCs, CuCs and CoCs catalysts. **Figures 2(a), (c) and (e)** show the evolution of N-species, *i.e.* $(1-X_{NO})$, N_2 and NO_2 concentration, together with X_{CB} ; **Figures 2(b), (d), and (f)** represent the evolution of CO and CO_2 in the experiments as well as X_{CB} . In all the catalyst, an initial N-species adsorption stage can be observed, taking place at temperatures from 250°C to 400°C , see **Figure 2(a), (c) and (e)**. No N_2 evolution was evidenced, fact that allows ascribing the observed reduction in the concentration of NO to its adsorption on the catalyst surface, almost neglecting the contribution of selective reduction of NO_x during this period. This adsorption stage is immediately followed by the desorption of N-species, mainly as

Table 1. Catalyst labeling, suspension viscosity at shear rate 1 s^{-1} and pH after 4 days ageing time, weight increase upon monolith coating and average thickness of the deposited catalytic layer.

| Catalyst | Viscosity (mPa·s) | pH | % weight increase after coating | Average layer thickness (μm) |
|----------|-------------------|-----|---------------------------------|---|
| CuCs | 2046 | 1.7 | 10.2 | 29 |
| CoCs | 1869 | 1.7 | 9.8 | 25 |
| FeCs | 3190 | 1.3 | 9.9 | 20 |

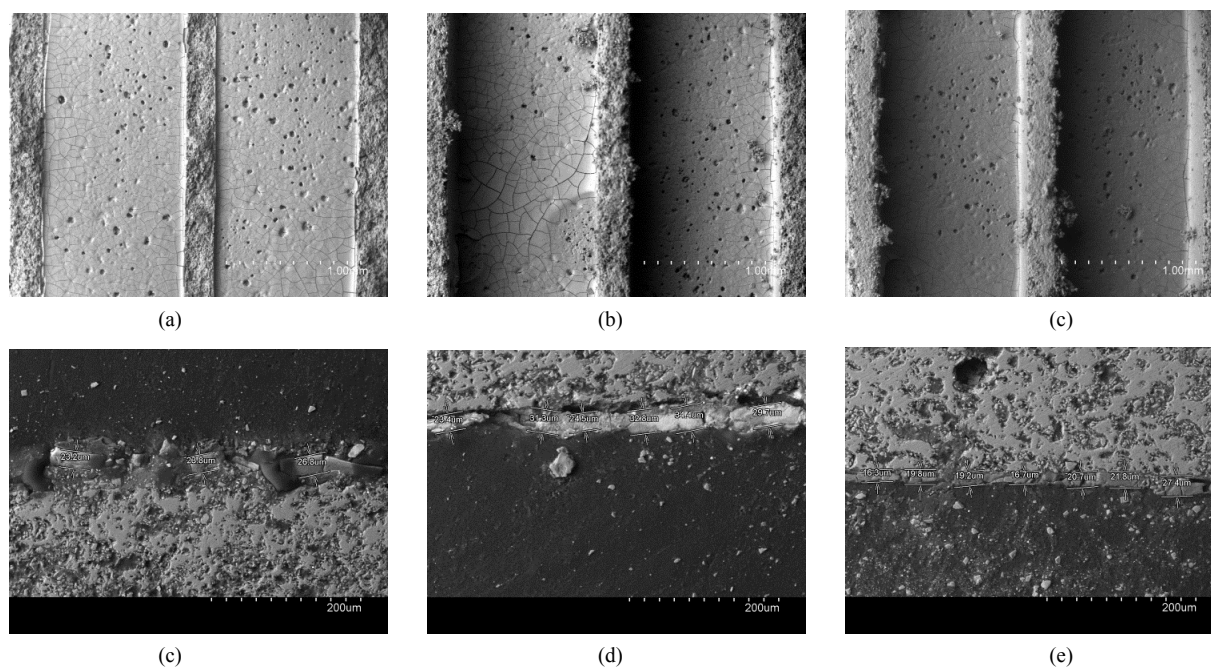


Figure 1. SEM images acquired for (a) and (d) CoCs, (b) and (e) CuCs, and (c) and (f) FeCs catalysts. Note: images (d), (e) and (f) correspond to cross sectional view of the catalysts, tangential to gas flow.

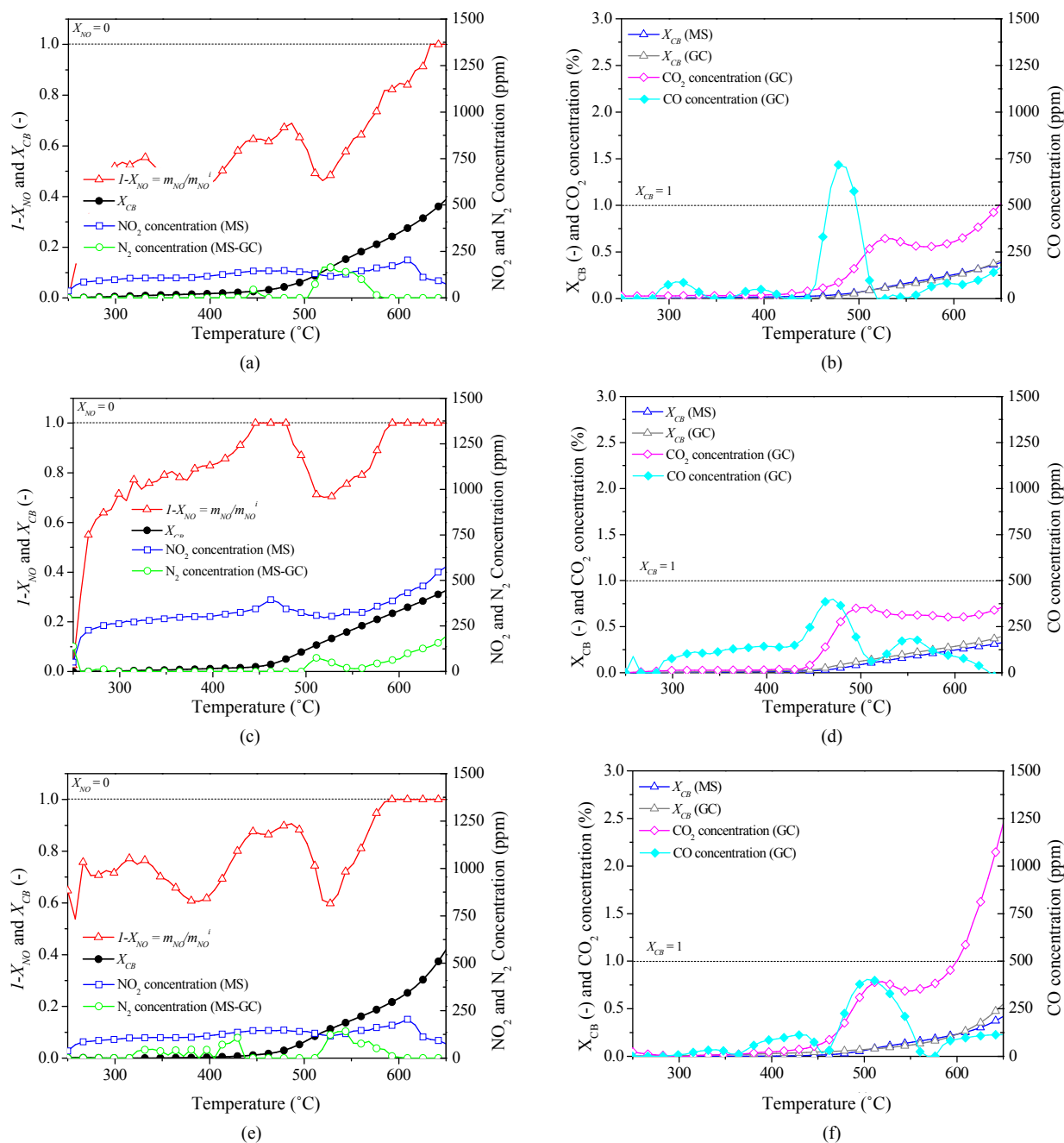


Figure 2. Simultaneous carbon black and NO_x removal experiments in the presence of the catalysts FeCs, (a) and (b); CuCs, (c) and (d) and CoCs (e) and (f).

Table 2. Textural characterization, surface area, S_{BET} , mesopore volume, V_{meso} , and average pore size, for the different catalysts prepared.

| Catalyst | S_{BET} (m ² /g) | V_{meso} (cm ³ /g) | Average pore size (nm) |
|----------|-------------------------------|---------------------------------|------------------------|
| CuCs | 9.7 | 0.021 | 7.4 |
| CoCs | 8.8 | 0.017 | 7.0 |
| FeCs | 10.1 | 0.021 | 7.6 |

NO. Only in the case of CuCs, **Figure 2(c)**, NO₂ evolution can be clearly observed. This fact points out principal to different adsorption mechanism taking place when using Cs as alkali promoter in comparison to preferable NO₂ desorption observed for K containing catalyst [27].

At 450°C carbon black oxidation sets off. In the same temperature window, 500°C - 600°C N-species are simultaneously reduced. NO conversion peaks at around 525°C in all the cases, reaching $X_{NO} = 0.55$ for FeCs catalyst, $X_{NO} = 0.42$ for CoCs catalyst whereas in the

case of CuCs, lower NO conversion was measured, $X_{NO} = 0.32$.

With respect to carbon black conversion, X_{CB} , **Figures 2(b), (d) and (f)** show evidence that it is partially non selective towards CO₂ in the lower temperature interval from 450°C to 550°C, as indicated by the measured CO evolution. At higher temperature, however CO₂ production prevails and almost no CO can be further measured. Maximal carbon black conversion reached at 650°C, is similar using FeCs and CoCs, $X_{CB} = 0.40$, and lower for CuCs, $X_{CB} = 0.30$.

In comparison to previous results obtained using K and Ba as alkali promoters [29] carbon black conversion is all the times lower in the presence of Cs-containing catalysts, moreover when compared to K-containing ones. This observation can be possible ascribed to different nitrogen species adsorption mechanism. When using K-containing catalysts NO₂ concentrations reached 1200 ppm. Preferable NO₂ evolution measured in the case of K-catalyst may result in enhanced carbon black oxidation, as previously reported in the existing literature [31].

4. Conclusions

Structured catalysts were prepared by means of coating cordierite monoliths with alumina-based suspensions containing transition metals (Cu, Co, Fe) and Cs as alkali promoter. Their activity was assayed in the simultaneous removal of soot and NO_x.

Coating led to the deposition of a catalytic layer of 20 - 29 μm average thickness. After coating, surface areas of the monoliths increased as a consequence of the deposition of the catalytic layer, which was mostly mesoporous and filled the macroporous structure of the original cordierite material.

Catalysts exhibited considerable deNO_x activity, reaching 55% conversion. The use of Cs as alkali promoter gave rise to low NO₂ evolution, resulting in lower activity towards soot oxidation for this system in comparison with previously studied K-containing catalyst. This fact may be assigned to different N-species adsorption mechanisms taking place in the presence of Cs, which must be further studied in detail.

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