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Catalytic filters for the simultaneous removal of soot and NO_x: Effect of CO_2 and steam on the exhaust gas of diesel engines

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ABSTRACT

Catalytic filters 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 V and K as the catalytically active phase. Textural and chemical properties of the coated monoliths were determined by means of N_2-physisorption, XRD, SEM-EDX and temperature programmed reduction. Activity of the catalytic filters in the simultaneous removal of soot and nitrogen oxides was tested in a fixed bed installation in absence and in presence of steam and CO_2. Complete soot oxidation was measured for some of the assayed catalytic filters, with high selectivity to CO_2 formation. NO reduction was preceded by a peak of NO_2 formation, which corresponded to maximum soot oxidation rate, pointing to the formation of NO_2 as a key step in the reaction mechanism for the simultaneous removal. Presence of steam and CO_2 diminished catalytic activity and selectivity for soot oxidation.

1. Introduction

Diesel engines' results in high emission of particulate matter i.e. soot; engine modifications have lowered these emissions, but still the use of after-treatment technologies is required to meet upcoming emission standards [1,2]. As soot, nitrogen oxides have a huge impact in atmospheric pollution; however, under typical operating conditions of diesel engines, three-way catalysts are not efficient in reducing NO_x [2,3]. NO_2 is highly reactive with soot, oxidizing it around 250 °C, typical of diesel engine exhausts during normal driving cycles. However, NO_2 concentrations in exhaust are normally low (5–15% of total NO_x), and not sufficient to provide high soot oxidation rates [4]. The "continuously regenerating-trap" (CRT) technology utilizes a Pt-supported catalysts upstream the particulate filter, allowing partial conversion of NO to NO_2, which subsequently reacts with the soot retained in the filter [5]. Substitution of this two-stage catalytic system by a single device [6], incorporates the catalyst on the surface of a filtering material. Based on the well known ability of carbonaceous materials to reduce NO_x, simultaneous removal, i.e. conversion of NO to NO_2, oxidation of soot and simultaneous reduction of NO_2 to N_2, has been successfully assayed, in the presence of $BaAl_2O_4$ [7], $CuFe_2O_4$ [8], K–Fe [9], K–Cu and K–Co [10] catalysts. The present study deals with the preparation of cordierite-based filters containing Me–K/Al_2O_3 (Me = Cu, Co, V) catalytic systems. Their activity in the simultaneous removal of soot and NO_x was assayed both, in the absence and in the presence of CO_2 and steam. Such compounds affect catalytic activity, via poisoning of the actives sites or dissolving the active phase present on the catalyst surface [11–13].

2. Materials and methods

Cylindrically shaped (1 cm diameter, 3 cm length) cordierite honeycomb monoliths ($2MgO{\cdot}2Al_2O_3{\cdot}5SiO_2$, Corning, 400 cpsi) were selected as catalyst support. Prior to impregnation, monoliths were subjected to oxidation in concentrated HNO_3. Alumina suspensions were prepared by sol–gel synthesis, using a highly dispersible boehmite (Disperal, Sasol), adding Cu, Co and V as catalytically active metals ($Cu(NO_3)_2{\cdot}3H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and NH_4VO_3 + oxalic acid), and K (KNO_3) as promoter. Concentrated nitric acid (65 wt.%) was added as peptizing agent. Several parameters were modified in the preparation of the suspensions, with the aim of evaluating their influence in the final suspension properties and monolith coating. Alumina load was varied from 4 to 6 wt.%, for 100 mL distillate water basis. Three different nitric acid to alumina, HNO_3/Al_2O_3, ratios were used, 0.04, 0.1 and 0.2. Metal to potassium, Me:K, ratio varied from 5:10, 10:5 to 10:10, all in wt.% with respect to the corresponding alumina load. Mixtures were stirred for 24 h, determining pH and viscosity. Coating was performed by forcing circulation of the suspensions through the channels of the monoliths, using a peristaltic pump. The

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Table 1
Description of the catalytic filters prepared and assayed, viscosity and pH of the suspensions used for filter coating, and weight increase measured after coating process.

Catalytic filter labelling	Coating suspension composition			Viscosity[a] (mPa s)	pH[b]	Weight increase after coating (%)
	% Al_2O_3	HNO_3/Al_2O_3	Me:K			
5/0.1/5:10/Cu	5	0.1	5:10	4770	3.2	12.2
5/0.1/10:10/Cu	5	0.1	10:10	5930	4.6	12.4
6/0.04/5:10/Cu	6	0.04	5:10	7180	3.4	9.6
5/0.1/5:10/Co	5	0.1	5:10	5300	3.2	10.5
5/0.1/10:10/Co	5	0.1	10:10	9340	3.3	10.6
4/0.2/10:10/V	4	0.2	10:10	2570	1.4	9.2

[a] Measured (Brookfield DV-E viscosimeter) after 24 h stirring, value at 1 s^{-1} shear rate.

[b] Measured (Crison GLP 21 + pH meter) after 4 days of ageing.

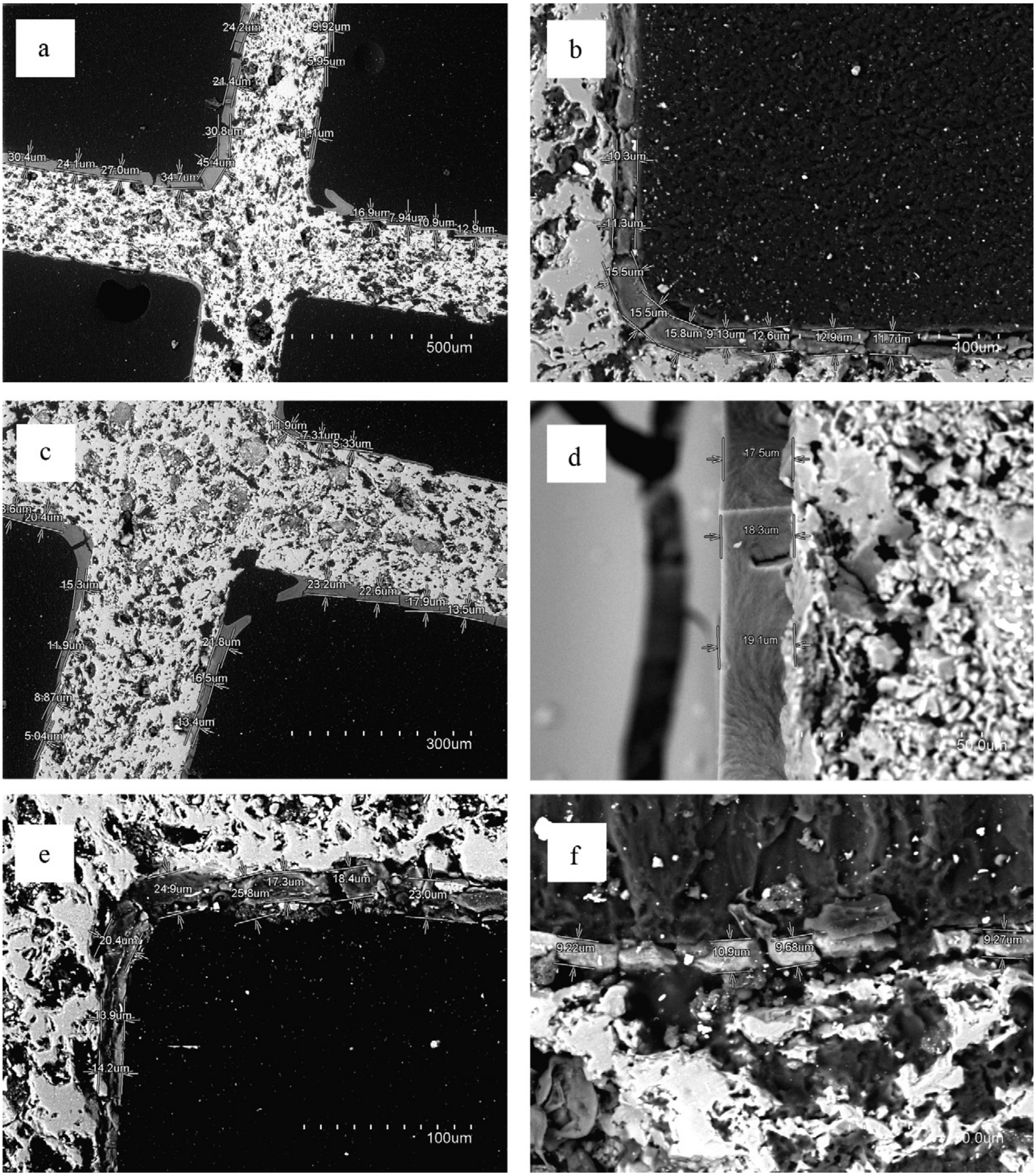

Fig. 1. SEM images for (a) 5/0.1/5:10/Cu, (b) 5/0.1/10:10/Cu, (c) 6/0.04/5:10/Cu, (d) 5/0.1/5:10/Co, (e) 5/0.1/10:10/Co and (f) 4/0.2/10:10/V catalytic filters.

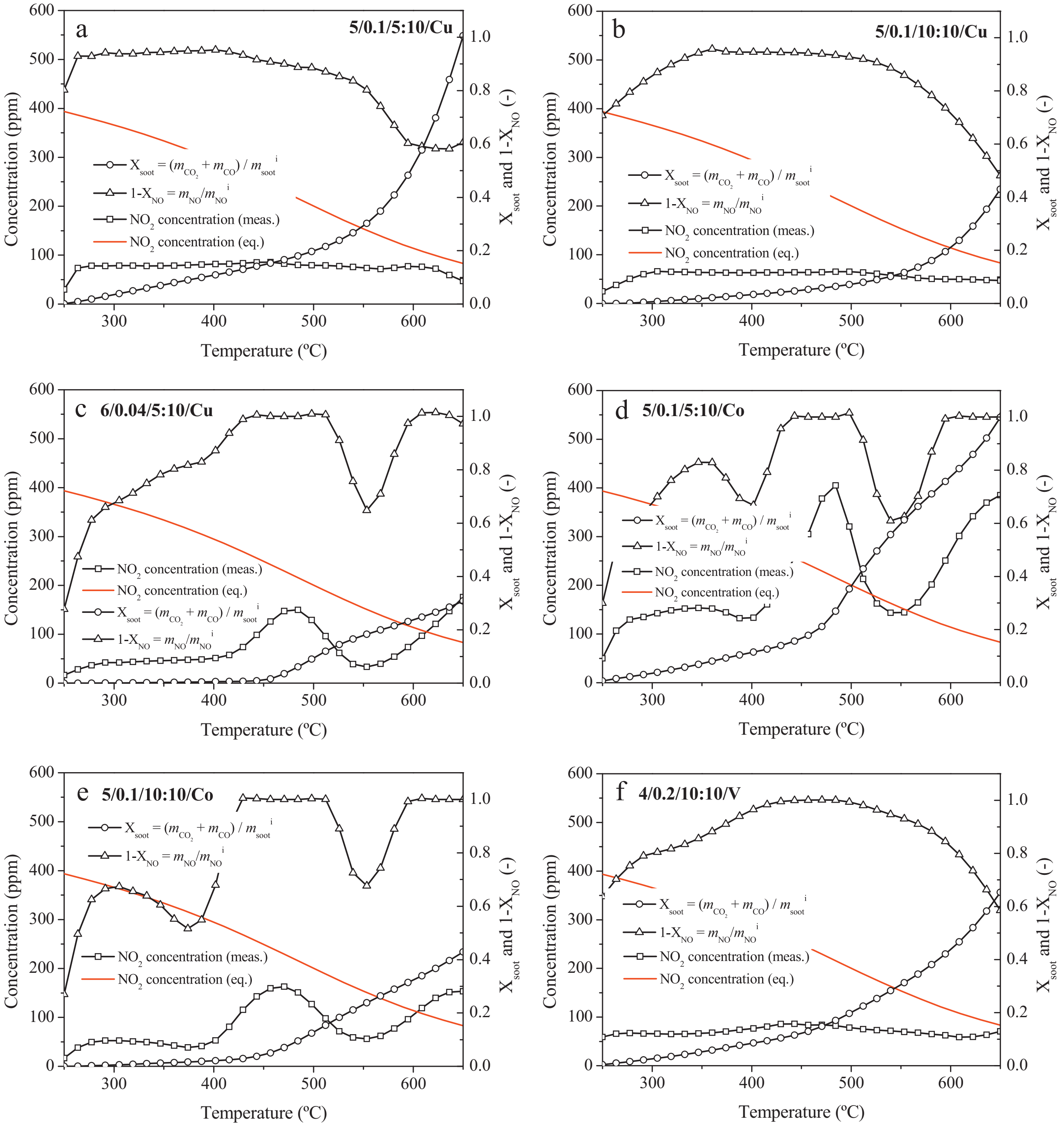

Fig. 2. NO_2 concentration, measured and equilibrium, soot conversion, X_{soot}, and NO reduction, X_{NO} measured during the simultaneous removal experiments in the presence of the catalysts presented in this work.

coated monoliths were flash-dried in flowing warm air (100 °C), dried overnight (108 °C), and subjected to calcination (450 °C, 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. A description of the assayed coated monoliths is provided in Table 1. The catalytic filters were characterized by X-ray diffraction (Bruker D8 Advance Series 2), SEM-EDX (Hitachi S-3400 N and Röntec XFlash), temperature-programmed reduction in H_2 (0.1 g catalyst, 50 mL/min 10% H_2–Ar, 25–950 °C, 5 K/min heating rate, TCD detector) and N_2 adsorption at −196 °C (Micromeritics ASAP 2020).

Channels in the monolith structure employed as support appear totally opened as the main goal of the present study was not to assay the soot filtration efficiency of the material but its catalytic activity in the simultaneous removal of soot and NO_x. Soot filtration was simulated instead, by incorporating carbon black (Elftex 430, Cabot), as model compound for diesel dry soot. The catalytic filters were soaked for 1 min in a carbon-black dispersion (0.2 g stirred at 200 rpm in 100 mL of n-pentane (95% pure)), removed and dried at 65 °C during 1 h. 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. [1,14].

The activity of the filters was tested in a fixed-bed lab-scale reactor. 50 mL/min reactant gas was flown through a 1 cm diameter by 3 cm length filter, gas residence time of 2.5 s, 0.12 s (corresponding to approximately 30,000 h^{-1} GHSV) taking into account the effective catalytic volume, for a monolith plus catalytic layer wall thickness of 30 μm. Temperature was raised at 5 K/min from 250 to 650 °C. Gas mixtures (in absence and in presence of steam and CO_2) tested to in catalytic activity assays were: (i) 600 ppmv NO and 5% O_2 in Ar, (ii) 600 ppmv NO and 10% O_2, 10% H_2O, 2% CO_2 in N_2, (iii) 600 ppmv NO and 10% O_2, 10% H_2O, 12% CO_2 in N_2, and (iv) 600 ppmv NO and 10% O_2, 12% CO_2 in N_2. Concentrations in the exiting gas were analyzed in a mass spectrometer (Balzers 422) and by gas chromatography (HP 5890).

3. Results and discussion

Coating suspensions were prepared by sol–gel method. As shown in Table 1, viscosities ranged from 2570 to 9340 mPa s, depending on composition while pH values stabilised around 3–4, corresponding to a lumina isoelectric point [15], except in the case of the V-containing suspension. Lower pH values in this case point to slower and more complex gelation process. As expected [16,17], higher alumina loads and higher acid concentrations led to gels of higher viscosity. Co-containing gels showed higher viscosities in comparison to Cu and V-containing gels, the latter being the less viscous in this series. Weight increase of the cordierite monoliths after coating was 10%, on average. Fig. 1 shows SEM images for Cu, Co and V coated monoliths; coating leaves a 10–20 μm thickness of catalytic layer on the monolith walls. Crack formation was observed, as a consequence of drying and calcination. Characterization of the catalytic filters by N_2-adsorption showed a significant increase of surface area and mesopore volume as a consequence of the deposition of the catalytic layer, which partially filled the macroporous structure of the original material. XRD characterization showed the transformation of the boehmite precursor into γ-Al_2O_3, after calcination. TPR-H_2 showed greater reducibility for the Co and Cu loaded monoliths than the V-loaded ones.

Fig. 2 shows the NO_2 concentration, both measured and corresponding equilibrium concentration, conversion for soot oxidation, X_{soot}, and the remaining NO fraction after reduction, $1 - X_{NO}$, from simultaneous removal experiments in the catalytic filters. Catalytic filters prepared with Cu and Co showed higher activity than the one prepared using V, both in NO reduction and soot oxidation. In the presence of 5/0.1/5:10/Cu catalytic filter, Fig. 2a, NO reduction starts at a temperature of 410 °C, reaching a maximum NO conversion of approximately 43% ($1 - X_{NO} = 0.57$) at 600 °C. Blank tests (absence of catalytic material) showed negligible NO reduction before 550 °C, reaching 22% conversion at 650 °C. With respect to soot removal, almost complete oxidation of the carbon black loaded in the 5/0.1/5:10/Cu catalytic filter was achieved, as compared to a maximum of 23% soot conversion in the blank tests. As the Cu content increases, NO reduction is enhanced but soot oxidation reaches a maximum conversion of only 43% (Fig. 2b). The V-containing catalytic filter, Fig. 2f, shows a similar behaviour to 5/0.1/5:10/Cu and 5/0.1/10:10/Cu filters. However, 6/0.04/5:10/Cu, 5/0.1/5:10/Co and 5/0.1/10:10/Co filters show two maxima of NO reduction, one at temperatures between 350 and 450 °C, followed by a second one around 500–600 °C. The second peak of NO reduction is preceded by a peak of NO_2 formation, which coincides at the same time with maximum soot oxidation rate. This fact points to NO_2 formation as the key step in the simultaneous removal process. It is worth noting that blank experiments in absence of both carbon black and catalytic material showed no peak of NO_2 evolution with an almost constant concentration of 100 ppm. At the sight of the equilibrium concentrations corresponding to the mixture of 600 ppm NO and 5% O_2, measured NO_2 concentration in these cases notably exceed the thermodynamically predicted oxidation of NO to NO_2. Presence of residual nitrates on the catalyst surface after its preparation can be neglected by both the results of the temperature programmed decomposition performed using the calcined catalyst powder and the blank tests. Thus, we can conclude that, most probably, at temperatures from 250 to 400 °C, NO is adsorbed in the catalyst surface, on K sites, generating nitrates which decompose at about 450 °C, in a similar way to what is claimed to occur in the presence of Pt-Ba catalyst for NO_x storage and reduction, NSR [18]. The catalytic filter 5/0.1/5:10/Co was able to oxidize all the carbon black initially loaded on its surface, reaching 39% NO conversion ($1 - X_{NO} = 0.61$) at 540 °C. NO reduction was found to be completely selective to N_2, whereas selectivity towards CO_2 in soot oxidation ranged from 71 to 94% for the Cu and Co-loaded catalysts, and a lower 56% for the V-containing filter.

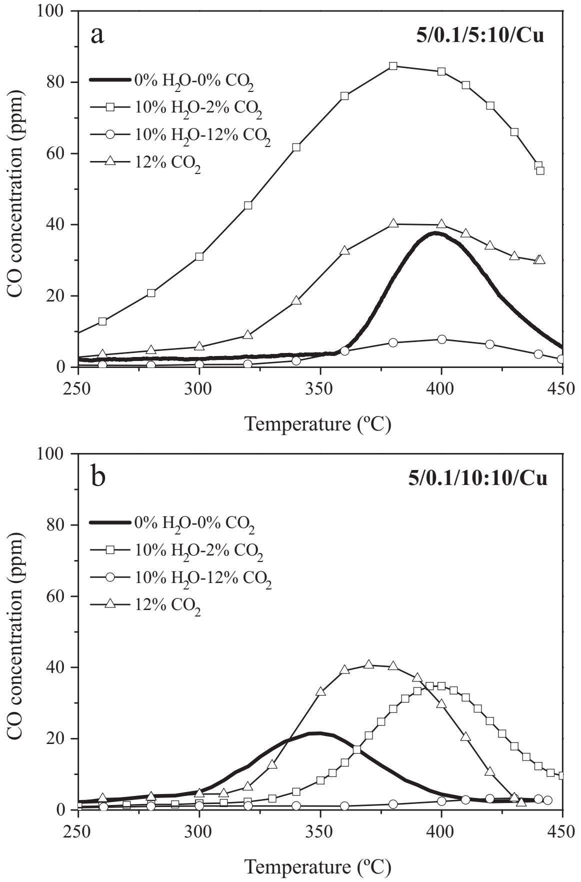

Fig. 3. CO evolution profiles determined during the simultaneous removal experiments in the presence of CO_2 and steam, for the catalytic filters (a) 5/0.1/5:10/Cu and (b) 5/0.1/10:10/Cu.

Fig. 3 shows CO concentration in the presence of CO_2 and steam, for the catalytic filters 5/0.1/5:10/Cu and 5/0.1/10:10/Cu. Presence of steam and CO_2 in the reactant gas mixture substantially influenced CO evolution at temperatures from 250 to 450 °C. For both catalysts, CO formation is enhanced in the presence of 10% H_2O–2% CO_2, but strongly inhibited in the presence of 10% H_2O–12% CO_2. The temperatures at which maximum evolution of CO takes place appear shifted to higher values, especially in the presence of the catalyst 5/0.1/10:10/Cu. Presence of both steam and CO_2 therefore caused a decrease in the catalytic activity towards soot oxidation or a substantial decrease in their selectivity. Competitive and, most probably, stronger CO_2 chemisorption on the catalyst surface might be responsible of the observed synergetic effect and consequent decrease in the soot oxidation ability in the presence of 10% H_2O–12% CO_2. If chemisorption occurs on Cu sites, this explanation further agrees with the even more dramatic deactivation observed for the catalytic filter 5/0.1/10:10/Cu. Nevertheless, additional research should be performed in order to clarify this fact, as well as its detailed influence in the catalytic activity and selectivity, i.e. by means of transient response analysis in the presence of several steam–CO_2 mixtures.

4. Conclusions

Catalytic filters prepared by coating cordierite monoliths with alumina-based suspensions containing Cu, Co or V and K as the catalytically active phase, showed outstanding activity in the simultaneous removal of soot and NO at temperatures between 250 and 650 °C.

Coating led to the deposition of a catalytic layer of 20 μm average thickness. Depending on suspension rheological properties, higher layer thicknesses were obtained, which resulted in less homogeneous coating, higher formation of cracks and even detachment of the layer in some areas of the cordierite monolith. 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. XRD characterization showed the transformation of the boehmite precursor into γ-Al_2O_3, after calcination. Temperature programmed reduction in the presence of H_2 showed increased reducibility for the Co and Cu loaded monoliths in comparison to V-loaded ones.

In absence of steam and CO_2, the Cu and Co catalytic filters showed higher activities in soot oxidation and NO reduction than the V-loaded ones. For some assays, soot oxidation was almost completed, whereas NO conversions around 40% were measured. Differences in the activity of the catalysts may be ascribed to different effective metal loadings after the deposition of the catalytic layer and its uniformity. Most active catalysts showed two maxima of NO reduction, first at temperatures around 400 °C followed by a second one at 500–550 °C. NO_2 formation took place during the dynamic experiments, at temperatures around 475–500 °C, preceding the second maxima of NO reduction and corresponding to a considerable increase in soot oxidation, pointing to NO_2 formation as a key step in the reaction mechanism of simultaneous removal. In the presence of steam and CO_2, catalytic activity in soot oxidation is hindered; CO formation is either shifted to higher temperatures or enhanced pointing to a less selective process in the presence of these compounds in the reactant gas mixture.

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References

[1] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Appl. Catal. B: Environ. 8 (1996) 57–78.
[2] D. Fino, N. Russo, C. Baldini, G. Saracco, V. Specchia, AIChE J. 8 (2003) 2173–2180.
[3] P. Ciambelli, P. Corbo, F. Migliardini, Catal. Today 59 (2000) 279.
[4] I.P. Kandylas, O.A. Haralampous, G. Koltsakis, Ind. Eng. Chem. Res. 41 (2002) 5372–5384.
[5] B.J. Cooper, J.E. Thoss, SAE Paper 890404, 1989.
[6] D. Mescia, J.C. Caroca, N. Russo, N. Labhsetwar, D. Fino, G. Saracco, V. Specchia, Catal. Today 137 (2008) 300–305.
[7] H. Lin, Y. Li, W. Shangguan, Z. Huang, Combust. Flame 156 (2009) 2063–2070.
[8] W.F. Shangguan, Y. Teraoka, S. Kagawa, Appl. Catal. B: Environ. 16 (1998) 149–154.
[9] K. Hizbullah, S. Kureti, W. Weisweiler, Catal. Today 93–95 (2004) 839–843.
[10] N. Nejar, M.J. Illán-Gómez, Appl. Catal. B: Environ. 70 (2007) 261–268.
[11] B.A.A.L. van Setten, C.G.M. Spitters, J. Bremmer, A.M.M. Mulders, M. Makkee, J.A. Moulijn, Appl. Catal. B: Environ. 42 (2003) 337–347.
[12] M.A. Peralta, V.G. Milt, L.M. Cornaglia, C.A. Querini, J. Catal. 242 (2006) 118.
[13] C. Badini, G. Saracco, V. Serra, V. Specchia, Appl. Catal. B: Environ. 18 (1998) 137–150.
[14] J.P.A. Neeft, M. Makkee, J.A. Moulijn, Appl. Catal. B: Environ. 12 (1997) 21–31.
[15] C. Cristiani, A. Grossale, P. Forzatti, Top. Catal. 42–43 (2007) 455–459.
[16] R.M. Heck, S. Gulati, R.J. Farrauto, Chem. Eng. J. 82 (2001) 149–156.
[17] C. Agrafiotis, A. Tsetsekou, J. Mater. Sci. 35 (2000) 951–960.
[18] M. Takeuchi, S. Matsumoto, Top. Catal. 28 (2004) 151–156.