Diesel soot combustion catalysts: a review of active phases.

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The most relevant information about the different active phases that have been studied for the catalytic combustion of soot has been reviewed and discussed in this article. Many catalysts have been reported to accelerate soot combustion, including formulations with noble metals, alkali and alkali earth metals, transition metals that can accomplish redox cycles (V, Mn, Co, Cu, Fe...) and internal transition metals. Platinum catalysts are among the most interesting for practical application, and one important feature of these catalysts is that sulfur resistant platinum formulations have been prepared. Some metal oxide-based catalysts seem also promising candidates for soot combustion in practical applications, including ceria-based formulations and mixed oxides with perovskite and spinel structures. Some of these metal oxide catalysts produce highly reactive active oxygen species that efficiently promote soot combustion. Thermal stability is one important requirement for a soot combustion catalyst, and this rules out the practical utilization of several potential catalysts like most alkali metal catalysts, molten salts and metal chlorides. Some noble metal catalysts are also unstable because they form volatile oxides (ruthenium, iridium and osmium).

Keywords: diesel soot; DPF; DOC; soot combustion catalyst; Pt catalyst; ceria; perovskite.

Introduction

Soot particles are emitted by Diesel engines together with NO_x, CO and unburned hydrocarbons (HC) in gas streams with high O₂, CO₂ and H₂O concentrations and temperatures typically below 500-550 °C. In these conditions, CO and HC oxidation can be easily accomplished in a Diesel Oxidation Catalyst (DOC), but both NO_x and soot need complex abatement strategies.

Diesel Particulate Filters (DPF) are used to remove soot particles from the exhaust stream (Neeft et al., 1996; Van Setten et al., 2001; Maricq, 2007; Twigg, 2007). This type of filters usually consist of wall-flow monoliths, that is, honeycomb-like structures with 50% of the channels plugged at the gas entrance side and the remaining channels plugged at the exit. The gas stream enters into the filter through the open channels, which is forced to pass through the porous walls where soot particles get stuck. DPF filters must be regenerated by soot combustion in order to avoid pressure drop in the exhaust, and there are several commercially available technologies for this purpose (Fino & Specchia, 2008).

The PSA system consists of using metal-fuel additives to obtain soot particles with catalytically active metals well embedded into the structure. A DPF is used to collect the metal catalyst-containing soot particles and, once filter regeneration is required, extra fuel is injected and its exothermic combustion starts the catalytic combustion of soot.

The Continuously Regenerating Trap (CRT) system (by Johnson Matthey) consists of a DPF filter located downstream a Pt-containing DOC catalyst. CO and HC are oxidized in the DOC, which also oxidizes NO to NO₂. NO₂ is much more oxidizing than NO and O₂ and rapidly reacts with soot and starts its ignition.

Some other filter regeneration strategies are being investigated, such as modifications of the CRT systems that incorporate active phases in the filter instead of or in addition to that in the previous oxidation catalyst or the Toyota Motors DPNR (Diesel Particulate NO_x Reduction) system for the simultaneous removal of NO_x and soot.

Intense research efforts are being done since the 1980s in order to design and improve soot combustion catalysts, and the goal of the current review article is to compile and discuss the most relevant information available about the different active phases that have been studied for the catalytic combustion of soot.

Table 1 compiles a survey about different active phases that have been tested for the catalytic combustion of soot. Comparison between soot catalytic combustion results obtained at different laboratories is not an easy task because of the particular features of the soot oxidation reactions:

- (i) Real soot is a heterogeneous material, and therefore, it is not convenient for catalysts screening. Important differences in the amount and type of ashes (sometimes metals with potential catalytic activity), amount of adsorbed hydrocarbons and degree of graphitization of the soot formed can be found. Usually, a model commercial carbon black is preferred for laboratory studies, and the behavior of a particular catalyst depends on the model carbon material used to perform the tests. Model carbon blacks typically have very low or null amounts of adsorbed hydrocarbons and metal compounds.
- (ii) The soot-catalyst contact strongly affects the catalytic combustion results, and it is not always easy to make sure that the contact in experiments performed at different laboratories is equal. It is generally accepted that “loose contact” mixtures of soot and powder catalysts (soot and catalyst are mixed with a spatula, for instance) are more convenient for laboratory experiments than “tight contact” mixtures (soot and catalyst are mixed in a mortar, for instance), because they are supposed to mimic the soot-catalyst contact in a real DPF much better (Van Setten et al., 2000). However, some authors screen their catalysts at laboratory in tight-contact with soot because differences in catalytic activity are more evident.
- (iii) Soot properties change with time during combustion (amount of oxygen, size and shape of the particles, graphitic structure, surface area, etc.). For this reason, the kinetic parameters of the catalyzed soot oxidation reactions (reaction rates, activation energies, pre-exponential factors...) also change with time, and they are only valid for very particular soot combustion conditions. This handicap has motivated that, in most articles devoted to the study of soot combustion catalysts, kinetic parameters are not reported.

95 In addition to these particular features of the soot combustion reactions, the reaction
96 rate also depends on general variables, such as, temperature for isothermal reactions and
97 heating rate for ramp experiments, nature and partial pressure of the gases in the stream, space
98 velocity/residence time of the gases in the solid bed, soot/catalyst ratio, etc. In order to restrict
99 the information spread on literature to results with a certain practical relevance, only data
100 obtained with catalysts tested in “loose contact” with soot and under both NO_x and O₂
101 containing gas mixtures have been considered in Table 1. However, in spite of these
102 precautions, it is not possible to achieve realistic conclusions about which catalyst is best and
103 which one is worst from data included in Table 1, and it is not the intention of this review
104 article to do it. The aim of the article is to compile the tremendous information available on
105 literature and to critically discuss this information identifying strong and weak points of each
106 type of catalyst.

107 According to the survey compiled in Table 1, many catalysts have been reported to
108 accelerate soot combustion, including formulations with noble metals (mainly Pt), alkali and
109 alkali earth metals, transition metals that can accomplish redox cycles (V, Mn, Co, Cu, Fe...) and
110 internal transition metals. In the coming sections of this article the most relevant
111 information reported about the behavior of the different type of soot combustion catalysts is
112 presented and discussed. The discussion is arranged in groups of catalysts according to their
113 composition or structure, that is, platinum catalysts, non-platinum noble metals and silver
114 catalysts, perovskites, spinels, ceria-based catalysts, metal chlorides, molten salts and alkali
115 metal catalysts.

Table 1. Compilation of soot combustion catalytic tests results. Only catalysts tested in “loose contact” with soot and under both NO_x and O₂ containing gas mixtures have been considered; only results obtained with fresh catalysts are included.

Catalysts	ΔT	$T_{\max}$	Relevant experimental details	Reference
SiO ₂		661		
1%Pt/SiO ₂		312	500 ml/min; 10% O ₂ + 7% H ₂ O + 1000 ppm NO + 100 ppm SO ₂ in N ₂ ; Flow reactor; 10 °C/min;	Oi-Uchisawa et al., 1998
1%Pt/Al ₂ O ₃		460	5 mg of soot + 500 mg catalyst; carbon black (Nippon Tokai carbon 7350F)	
1%Pt/ZrO ₂		408		
SiO ₂		687		
1%Pt/SiO ₂		562		
V ₂ O ₅ /SiO ₂		555	500 ml/min; 1000 ppm NO + 10% O ₂ + 7% H ₂ O in N ₂ ; Flow reactor; 10 °C/min; 5 mg of soot +	Liu et al., 2001
V ₂ O ₅ -Pt/SiO ₂		518	500 mg catalyst; carbon black (Nippon Tokai carbon 7350F)	
MoO ₃ /SiO ₂		535		
MoO ₃ -Pt/SiO ₂		475		
γ -Al ₂ O ₃ (260 m ² /g)		~650		
1%Pt/ γ -Al ₂ O ₃ (210 m ² /g)		~550	100 ml/min; 2000 ppm NO _x + 5% O ₂ in He; Flow reactor; 15 °C/min; 66 mg (1:9 soot:catalyst);	Castoldi et al., 2006
1%Pt/20%Ba/ γ -Al ₂ O ₃ (160 m ² /g)		~580	Printex U.	
2.5%Pt/4%K ₂ O/Al ₂ O ₃	150	375	200 ml/min; 600 ppm NO _x + 10% O ₂ in Ar; Flow reactor; 1 °C/min; 100 mg (1:4 soot:catalyst); 43000 h ⁻¹ ; Printex U.	Krishna & Makkee, 2006
Cs ₂ SO ₄ ·V ₂ O ₅ /foam filter		~475		
1%Pt/Al ₂ O ₃		~415	200 ml/min; 600 ppm NO _x + 10% O ₂ in Ar; Flow reactor; 0.6 °C/min Printex U.	Setiabudi et al., 2002
Ce _{0.8} Zr _{0.2} O ₂ (3DOM)	191	394		
1%Pt/Ce _{0.8} Zr _{0.2} O ₂ (3DOM)	231	354	50 ml/min; 2000 ppm NO + 5% O ₂ in Ar; Flow reactor; 2 °C/min; 10 mg of soot + 100 mg	Wei et al., 2013
8%Pt/Ce _{0.8} Zr _{0.2} O ₂ (3DOM)	259	326	catalyst; Printex U.	
CeO ₂ (64 m ² /g)	88	518		
Ce _{0.76} Zr _{0.24} O ₂ (67 m ² /g)	85	521		
Ce _{0.56} Zr _{0.44} O ₂ (31 m ² /g)	19	587	500 ml/min; 500 ppm NO _x + 5% O ₂ in N ₂ . Flow reactor; 10 °C/min; 100 mg (1:4 soot:catalyst);	Atribak et al., 2009
Ce _{0.36} Zr _{0.64} O ₂ (8 m ² /g)	10	596	30000 h ⁻¹ ; Printex U.	
Ce _{0.16} Zr _{0.84} O ₂ (47 m ² /g)	0	606		
ZrO ₂ (65 m ² /g)	24	582		
CeO ₂ (49 m ² /g)	129	465		
Ce _{0.8} Sm _{0.2} O ₂ (47 m ² /g)	128	466	50 ml/min; 2000 ppm NO _x + 5% O ₂ in He; Flow reactor; 1 °C/min.; 100 mg (1:10 soot:catalyst);	Liu et al., 2011
Ce _{0.8} Zr _{0.2} O ₂ (48 m ² /g)	125	469	Printex U.	
Ce _{0.8} V _{0.2} O ₂ (15 m ² /g)	100	494		
Ce _{0.5} Zr _{0.5} O ₂ (132 m ² /g)		500	500 ml/min; 10%O ₂ + 1000 ppm NO + 7%H ₂ O in N ₂ . Flow reactor; 10 °C/min; 5 mg of soot + 100 mg catalyst; Printex U.	Zhu et al., 2007

Catalysts	ΔT	$T_{\max}$	Relevant experimental details	Reference
CeO ₂ (2 m ² /g)	54	474	200 ml/min; 600 ppm NO _x + 10% O ₂ in Ar; Flow reactor; 0.6 °C/min; 100 mg (1:4 soot:catalyst); 70000 h ⁻¹ ; Printex U.	Krishna et al., 2007b
Ce _{0.9} La _{0.1} O _x (16 m ² /g)	68	460		
Ce _{0.9} Pr _{0.1} O _x (11 m ² /g)	109	419		
Ce _{0.9} Sm _{0.1} O _x (5 m ² /g)	35	493		
Ce _{0.9} Y _{0.1} O _x (2 m ² /g)	24	504		
Pt/Al ₂ O ₃ (comercial)		~515	140 ml/min; 10% O ₂ + 1000 ppm NO + 3%H ₂ O in N ₂ ; TGA reactor; 10 °C/min; 5 mg of soot + 100 mg catalyst; Real soot.	Tikhomirov et al., 2006
CeO ₂ (37 m ² /g)		~550		
Mn _{0.25} Ce _{0.75} O _x (86 m ² /g)		~460		
Mn _{0.50} Ce _{0.50} O _x (79 m ² /g)		~590		
Mn _{0.75} Ce _{0.25} O _x (89 m ² /g)		~500		
Mn ₂ O ₃ (24 m ² /g)		~585	500 ml/min; 1000 ppm NO + 9.5% O ₂ in N ₂ ; Flow reactor; 20 °C/min; 5 mg of soot + 100 mg catalyst; Printex U.	Wu et al., 2007
CeO ₂ (62 m ² /g)		~465		
CuO-CeO ₂ (68 m ² /g)		~420		
CeO ₂ -ZrO ₂ (57 m ² /g)		~478		
CuO-CeO ₂ -ZrO ₂ (51 m ² /g)		~448		
La ₂ CuO ₄		504	50 ml/min; 2000 ppm NO+ 5% O ₂ in He; Flow reactor; 2 °C/min; 108 mg (1:5 soot:catalyst) Flow reactor; Printex U.	Liu et al., 2008
Pr ₂ CuO ₄		507		
Nd ₂ CuO ₄		518		
Sm ₂ CuO ₄		518		
Gd ₂ CuO ₄		520		
La _{1.3} Na _{0.7} CuO ₄		463	500 ml/min; 500 ppm NO _x + 5% O ₂ in N ₂ ; Flow reactor; 10 °C/min; 100 mg (1:4 soot:catalyst); 30000 h ⁻¹ ; carbon black (Vulcan XC72)	Zawadzki et al., 2009
ZnAl ₂ O ₄ (133 m ² /g)	35	630		
5% CuO/ZnAl ₂ O ₄ (111 m ² /g)	65	600		
Zn _{0.95} Cu _{0.05} Al ₂ O ₄ (148 m ² /g)	18	647	500 ml/min; 500 ppm NO _x + 5% O ₂ in N ₂ ; Flow reactor; 10 °C/min; 100 mg (1:4 soot:catalyst); 30000 h ⁻¹ ; carbon black (Vulcan XC72)	López-Suárez et al., 2009
K-Cu/SrTiO ₃ (9 m ² /g)	188	495		
Sr _{0.8} K _{0.2} TiO _x (5 m ² /g)	215	468		
K/SrTiO ₃ (7 m ² /g)	195	488		
Cu/SrTiO ₃ (11 m ² /g)	78	605	50 ml/min; 2000 ppm NO _x + 5% O ₂ in He; Flow reactor; 2 °C/min; 180 mg (1:5 soot:catalyst)	Wang et al., 2008
LaCoO ₃ (9 m ² /g)	178	421		
La _{0.90} K _{0.10} CoO ₃ (11 m ² /g)	201	398		
LaFeO ₃ (3DOM)	153	432	50 ml/min; 2000 ppm NO + 5% O ₂ in Ar; Flow reactor; 2 °C/min; Printex U.	Xu et al., 2010
LaCo _{0.5} Fe _{0.5} O ₃ (3DOM)	188	397		
LaMn _{0.95} Fe _{0.05} O ₃ (3 DOM)		392	50 ml/min; 2000 ppm NO + 5% O ₂ in Ar; Flow reactor; 2 °C/min; Printex U.	Zheng et al., 2012

¹²⁰ ΔT : Difference between the un-catalyzed and catalyzed soot combustion temperatures (°C).

¹²¹ $T_{\max}$: Temperature of maximum soot combustion rate, maximum CO_x emission or temperature for 50% soot conversion (°C).

Platinum catalysts

Pt is being currently used in soot removal commercial systems. The so-called CRT (Continuously Regenerating Trap) system, which is already used on heavy duty diesel vehicles such as trucks and buses, utilizes a platinum-containing DOC in front of a DPF filter to control HC and CO emissions, and also to oxidize NO to NO₂ for low temperature combustion of soot in the downstream filter when driving conditions are appropriate for this to take place (Twigg, 2006, 2007).

The role of platinum on the combustion of soot with O₂ has been postulated to be the spillover of activated oxygen (Neri et al., 1997) and, on NO_x/O₂ mixtures, the catalytic oxidation of NO to NO₂ (Setiabudi et al., 2002). In presence of both NO₂ and O₂, it has been also reported (Jeguirim et al., 2007) that besides the well-established catalytic oxidation of NO into NO₂, Pt also has a catalytic effect on the cooperative carbon–NO₂–O₂ oxidation reaction. An overall mechanism involving the formation of atomic oxygen over platinum sites followed by its transfer to the carbon surface has been proposed. It has been suggested that platinum catalysts increase the surface concentration of surface carbon oxygen complexes which then react with NO₂ leading to an enhanced carbon consumption.

The effect of the support oxide and platinum precursor on the catalytic combustion of soot oxidation was studied in a simulated exhaust gas with N₂, O₂, H₂O, NO and SO₂ (Oi-Uchisawa et al., 1998). The platinum precursors compared were Pt(NH₃)₄(OH)₂, H₂PtCl₆·6H₂O, Pt(NH₃)₄(NO₃)₂, and Pt(NH₃)₄Cl₂ and the supports tested were SiO₂, Al₂O₃, and ZrO₂. Pt/SiO₂ prepared from Pt(NH₃)₄(OH)₂ showed the highest carbon oxidation activity, and it was observed that platinum dispersion did not explain the catalytic trends. The soot combustion activity was only related to the catalytic oxidation of NO to NO₂. In a later study (Oi-Uchisawa et al., 2000), the effect of support materials for platinum catalysts on the oxidation of carbon black was revisited, and several platinum-supported metal oxides were evaluated (Ta₂O₅, Nb₂O₅, WO₃, SnO₂, SiO₂, TiO₂, Al₂O₃ and ZrO₂). Pt/Ta₂O₅ showed the highest activity in a model diesel exhaust containing O₂, H₂O, NO and SO₂ in N₂. Platinum catalysts supported on other non-basic metal oxides such as Nb₂O₅, WO₃, SnO₂ and SiO₂ showed similar high activities. The high activity for these catalysts was attributed to their non-basicity and negligible affinity toward SO₃ (or H₂SO₄), which resulted in less poisoning of the supported platinum. The MO_x supports used for platinum catalysts were further improved by using MO_x-TiO₂ mixtures (Oi-Uchisawa et al., 2003), and highest activities

were obtained with Pt/(TiO₂+SiO₂) for molar ratios of TiO₂/(TiO₂+SiO₂) in the range 0.4 to 0.7. This improvement was attributed to the enhanced sulfur resistance.

Synergetic effect between platinum and some other active components has been reported as well. A series of SiO₂-supported MoO₃, V₂O₅, and/or platinum catalysts were investigated (Liu et al., 2001), concluding that catalysts with both platinum and metal oxides were more active than the single-component catalysts. A synergistic reaction mechanism was suggested to explain the effects of combining platinum with the oxides, where platinum catalyzes the oxidation of NO with gas phase O₂ to NO₂, while MoO₃ and V₂O₅ catalyze the oxidation of carbon with NO₂. Jelles et al. (1999a) also reported a synergetic effect between platinum, used as post-combustion catalyst, and cerium introduced into the soot structure by using a fuel additive. The high soot combustion rate was explained by a cycle of two catalytic reactions, where platinum oxidizes NO to NO₂, which subsequently oxidizes soot using cerium as a catalyst, forming NO which can participate in the reaction more than once.

Recently, three-Dimensionally Ordered Macroporous (3DOM) Ce_{0.8}Zr_{0.2}O₂-supported platinum catalysts have been synthesized (Wei et al., 2013). It has been proposed that the 3DOM structure improves the contact efficiency between catalyst and soot, and the metal (Pt)-support (Ce) synergistic effect increases the amount of active oxygen species delivered to soot. 3DOM Pt/Ce_{0.8}Zr_{0.2}O₂ catalysts exhibited high catalytic activity and thermal stability for soot combustion.

The synergistic effect between platinum and magnesium (Liu et al., 2012) has been also reported to enhance the NO oxidation activity and NO_x storage capacity of Pt-Mg/Al₂O₃ catalyst. More NO₂ is produced in the temperature range of soot oxidation on Pt-Mg/Al₂O₃ than on a Mg-free Pt/Al₂O₃ catalyst with a similar Pt particle size, which efficiently promotes the ignition of soot.

Soot combustion on NSR (NO_x Storage and Reduction) catalysts has recently attracted attention (Castoldi et al., 2006; Krishna & Makkee, 2006; Kustov et al., 2009; Matarrese et al., 2009; Pieta et al., 2010; Klein et al., 2012), in order to evaluate the potential simultaneous removal of NO_x and soot (DPNR systems; Diesel Particulate NO_x Reduction) and to check the effect of soot in NSR catalysts performance. NSR catalysts typically combine platinum with a basic oxide/carbonate (alkali or alkali earth metal oxides/carbonates) and operate in cycles of O₂-rich and O₂-lean atmospheres. NO_x are chemisorbed on the basic compounds during the O₂-rich cycles and are reduced during the lean periods attained by extra diesel injection.

188 The potential utilization of a typical Pt–Ba/Al₂O₃ NSR catalyst for the simultaneous
 189 removal of soot and NO_x was investigated and compared with that of a Pt/Al₂O₃ sample
 190 (Castoldi et al., 2006). It was found that the Pt–Ba/Al₂O₃ catalyst was able to simultaneously
 191 remove both soot and NO_x while the Pt/Al₂O₃ catalyst effectively performed the soot
 192 oxidation but was not able to remove gas phase NO_x to a significant extent. These authors
 193 observed that the presence of soot did not significantly affect NO_x reduction on the Pt–
 194 Ba/Al₂O₃ catalyst (Castoldi et al., 2006). On the contrary, Klein et al. (2012) also studied the
 195 effect of soot on the performance of PtBa/Al₂O₃ NSR catalysts and reported that the presence
 196 of soot in the catalytic bed leads to the decrease of the NO_x storage capacity (NSC) of the
 197 catalysts. Participation of a direct reaction between carbon particles and NO_x storage sites to
 198 form carbonate adsorbed species was proposed. However, the loss of NSC measured in the
 199 presence of carbon varied as a function of the catalyst composition. It was shown that the
 200 presence of platinum limited the influence of carbon–catalyst contact. The proximity between
 201 the storage sites, platinum sites and their contact with carbon seems to be a key factor. During
 202 the carbon oxidation process, catalysts aging caused by platinum sintering and Ba
 203 agglomeration seems to occur. These structural modifications reduce the proximity between
 204 the platinum and adsorption sites (Ba and/or Al), which results in a decrease in the NO_x
 205 storage capacity (Klein et al., 2013).

206 Soot oxidation activity and deactivation of NSR catalysts containing Pt, K, and Ba
 207 supported on Al₂O₃ were also studied (Krishna & Makkee, 2006). The NSR catalysts were
 208 active to accelerate soot combustion, and the reactions that were mainly responsible of such
 209 activity where soot oxidation with NO₂ followed by NO recycle to NO₂, and soot oxidation
 210 with O₂ assisted by NO₂. Only a part of the stored NO_x that was decomposed at high
 211 temperatures under lean conditions was found to be useful for soot oxidation. NO_x storage
 212 capacity of these NSR catalysts decreased upon aging under soot oxidizing conditions. Pt/K–
 213 Al₂O₃ catalyst was more active, but least stable compared with Pt/Ba–Al₂O₃ because the
 214 active species responsible for synergism on Pt/K–Al₂O₃ are unstable and cannot be
 215 regenerated (Krishna & Makkee, 2006). It has been also proposed (Matarrese et al., 2013) the
 216 direct participation of the surface nitrates in soot oxidation on Pt/K–Al₂O₃ NSR catalysts,
 217 without the requirement of the preliminary thermal decomposition of nitrates. Such a
 218 mechanism was proposed to occur thanks to the mobility of the adsorbed NO_x species and is
 219 not promoted by platinum. This surface reaction mechanism parallels the gas-phase soot
 220 oxidation by NO₂ and O₂ evolved upon decomposition of the stored NO_x. Potassium-based

catalysts are more active than Ba-containing catalysts due to the higher mobility of the NO_x species adsorbed on potassium with respect to barium.

Non-platinum noble metals and silver catalysts

Non-platinum noble metals have not been studied very often as soot combustion catalyst, and few articles have been reported regarding the study of silver catalysts.

Na-Y zeolite-supported iridium, palladium, platinum, and rhodium metals were screened as carbon oxidation catalysts, and ruthenium was proposed to be the most active noble metal (Villani et al., 2006). However, it is known that ruthenium (and also iridium and Osmium) form volatile oxides, which rules out its practical utilization (Gandhi et al., 2003).

Au–V-based catalysts have been studied for soot combustion with special attention to the reaction mechanism (Van Craenenbroeck et al., 2002). Gold particles do provide very active sites able to ignite soot within the desired temperature range but retard the oxidation process at high vanadium loadings because of the diminished contact. Gold particles were proposed to promote the oxygen transfer from catalyst to soot, which increases the activity in the combustion of soot particles. This positive effect could become negative because the same oxygen donor property might be responsible for the formation of polyvanadate clusters instead of V₂O₅ crystallites, diminishing the mobility of the catalyst.

The effect of 2% gold addition to LaBO₃ perovskite catalysts (B = Cr, Mn, Fe and Ni) was also studied in the simultaneous CO and soot combustion (Russo et al., 2008). The comparison of their activity with those of the corresponding gold-free pure perovskite evidenced that the presence of gold had a good synergetic effect towards CO oxidation and a negligible one towards carbon combustion.

Soot combustion over silver-supported catalysts was studied by using Al₂O₃, CeO₂ and ZrO₂ supports (Aneggi et al., 2009). Formation of Ag/Ag₂O mixtures was observed in all supports and their relative abundance is strictly correlated to the nature of the support. Ceria was shown to stabilize silver oxide while with ZrO₂ and Al₂O₃ metallic silver was preferentially formed. For this reason, it was proposed that Ag/ZrO₂ and Ag/Al₂O₃ were active catalysts while the bare ZrO₂ and Al₂O₃ supports were not. On the contrary, silver addition to ceria had little benefit, because ceria itself is active in soot oxidation and silver forms a low active oxide. However, it has been recently reported the preparation of very active Ag/CeO₂ catalyst with a novel structure which consist of aggregates of ceria particles

around a central silver metal core (Kayama et al., 2010). It is proposed that such rice-ball nanostructure produces extremely active oxygen.

Perovskite catalysts

ABO₃ perovskite-type oxides (with A = La+Sr, La+Li, La+K or La+Cs and B = Co, Mn, Fe, Mn+Fe, Mn+Cu or Cu+V) catalyzed the simultaneous removal of NO_x and diesel soot in the presence of oxygen, and were superior to transition metal simple oxides in the selectivity for NO_x reduction (Teraoka et al., 1995). The catalytic activity of perovskite-type oxides depended on both A-site and B-site cations, and incorporation of potassium at A sites prominently promoted the oxidation of soot and the reduction of NO_x. La_{1-x}K_xMnO₃ perovskite catalysts were also tested for the simultaneous removal of NO_x and soot (Teraoka et al., 2001). The solubility limit of potassium in these mixed oxides was determined to lie between x=0.2 and x=0.25, and the activity and NO_x reduction selectivity for N₂ depended significantly on the potassium content, being highest for compositions close to the solubility limit. ABO₃ perovskites with A= La+K and B = Cu+V were also effective for the simultaneous removal of soot and NO_x at 450–500 °C, but the stability at high temperature (800 °C) was poor (Fino et al., 2003).

LaCrO₃, LaFeO₃ and LaMnO₃ perovskite catalysts were compared, and the highest activity for soot combustion of the chromite catalyst was related to its highest concentration of suprafacial, weakly chemisorbed oxygen, which contributes actively to soot combustion by spillover in the temperature range 300–500°C (Fino et al., 2003b). Lithium introduction on chromium position of LaCrO₃ soot combustion perovskite catalysts has shown to improve the activity due to the enhancement of the amount of weakly chemisorbed oxygen O⁻ species (Fino et al., 2006b). The simultaneous introduction of potassium on lanthanum position and copper on manganese position of the LaMnO₃ perovskite also enhanced the catalytic behavior (Peng et al., 2007), and also the partial substitution of lanthanum by alkali metal cations (Wang et al., 2008; Russo et al., 2008b) and cobalt by palladium (Yao 2009) on LaCoO₃.

Hirano et al., (2009) studied strontium-substituted LaFeO₃ perovskites for soot combustion, and the activity of these perovskites was reported to be only slightly lower to that of a Pt/Al₂O₃ reference catalyst. Teraoka et al., (1996) also reported that Co, Mn and Fe perovskite-type and Cu-based K₂NiF₄-type oxides (all with La³⁺ partially substituted by alkali or alkali metal cations) catalyze the simultaneous removal of NO_x and diesel soot particulate

287 and that these perovskite related oxides are superior to transition metal simple oxides and
288 Pt/Al₂O₃ with respect to the selectivity to NO_x reduction.

289 SrTiO₃ perovskites doped with alkaline compounds were studied by Białobok et al.,
290 (2007) for soot combustion, and the activity increased in the following order of alkali metals:
291 SrTiO₃ < Li/SrTiO₃ < Cs/SrTiO₃ < K/SrTiO₃. It was also concluded that substitution
292 produced catalysts with higher activity than catalysts with similar composition but prepared
293 by impregnation. However, the activity for soot combustion in NO_x/O₂ of potassium
294 impregnated and substituted SrTiO₃ perovskite catalysts was studied, concluding that fresh
295 catalysts are active but they are progressively deactivated due to the loss of potassium during
296 consecutive reaction cycles (López-Suárez et al., 2009).

297 The promoting effect of impregnated copper on the SrTiO₃ perovskite activity for the
298 catalytic combustion of soot has been also reported. The higher activity of Cu/SrTiO₃ in
299 comparison to Cu/Al₂O₃ was attributed to the improved redox properties of copper originated
300 by Cu-support interactions, which improve the catalytic oxidation of NO to NO₂. This seems
301 to be related to the presence of weakly bound oxygen on this sample, since copper species
302 present on the Cu/SrTiO₃ catalyst were reduced more easily than those in other inert supports
303 (López Suárez 2008).

304 Recently, several three dimensionally ordered macroporous (3DOM) solids are being
305 investigated as soot combustion catalyst, some of them based on perovskite structures. Xu et
306 al. (2010) have prepared LaCo_xFe_{1-x}O₃, Zhang et al. (2010b) prepared La_{0.9}K_{0.1}CoO₃ and
307 Zheng et. al. (2012) prepared LaMn_{1-x}Fe_xO₃.

308 Several perovskite catalysts have been coated on particulate filters and the
309 regeneration has been evaluated. The PrCrO₃ perovskite supported on CeO₂ was loaded on
310 catalytic wall-flow trap and pilot plant tests were carried out on a diesel engine bench (Fino &
311 Specchia 2004). The authors suggested that this formulation improved the performance of
312 Pt/Al₂O₃ catalysts.

313 The La_{0.8}Ce_{0.2}MnO₃ perovskite has been used for the microwave-assisted in-situ
314 regeneration of diesel soot filters (Zhang-Steenwinkel et al., 2005). This perovskite has
315 suitable dielectric properties, i.e., a high dielectric loss factor, and simultaneously acts as an
316 oxidation catalyst. The advantage of microwaves heating with regard to conventional thermal
317 heating is that it is a bulk heating technique, and therefore, it is fast and selective. A
318 monolithic soot filter coated with a La_{0.8}Ce_{0.2}MnO₃ perovskite was fully microwave –assisted
319 regenerated with almost 100% selectivity towards CO₂. In contrast, the same filter without

such a coating was only partially regenerated, and considerable amounts of CO were formed. The $\text{La}_{0.8}\text{Ce}_{0.2}\text{MnO}_3$ coating showed excellent temperature shock resistance and thermochemical stability and the authors proposed that, once a suitable microwave cavity is designed, microwave assisted soot filter regeneration would be feasible.

However, formation of perovskite structures not always has a positive effect on the soot combustion activity of mixed oxides, and few examples of catalyst deactivation due to perovskite structure formation have been reported. The stability of Ba,K/CeO₂ catalysts, which have been shown to be very active for soot combustion, was studied and, above 830°C, catalyst deactivation due to BaCeO₃ perovskite structure formation was observed (Peralta et al., 2006).

Spinel catalysts

Shangguan et al. (1996) studied the simultaneous removal of NO_x and diesel soot particulate in the presence of excess oxygen with ternary AB₂O₄ spinel oxides. The catalytic performance depended significantly on the metal cations used, and CuFe₂O₄ was the best catalyst. The performance of this spinel catalyst was much better than that of the mechanical mixtures of the metal oxides. This conclusion was also extended to Cu-Cr systems.

Nanostructured spinel-type oxide catalysts AB₂O₄ (where A = Co and Mn, and B = Cr and Fe) have also demonstrated to be effective for the simultaneous removal of soot and NO_x (Fino et al., 2006). The activity order for soot combustion was found to be $\text{CoCr}_2\text{O}_4 > \text{MnCr}_2\text{O}_4 > \text{CoFe}_2\text{O}_4$, whereas the activity order for NO_x reduction was $\text{CoFe}_2\text{O}_4 > \text{CoCr}_2\text{O}_4 > \text{MnCr}_2\text{O}_4$. The best compromise between simultaneous abatement of soot and nitrogen oxide was therefore shown by the CoCr₂O₄ catalyst, which could promote soot combustion and appreciable NO_x reduction below 400 °C. The prevalent catalytic combustion activity of the chromite catalysts could be explained by their higher concentration of suprafacial, weakly chemisorbed oxygen, which contributes actively to soot combustion by spillover. A CoAl₂O₄ spinel catalyst has also shown an activity for soot combustion reaction similar to that of a Pt/Al₂O₃ reference catalyst (Zawadzki et al., 2011). This high soot combustion activity of CoAl₂O₄ was attributed to its high NO_x chemisorption capacity, what allowed fast NO oxidation to NO₂.

BaAl₂O₄ spinel was also proved to be an effective to catalyze the reaction between soot and NO_x under lean-burn condition, promoting the simultaneous NO_x reduction to N₂ and soot oxidation to CO₂ (Lin et al., 2009). The interaction of nitrates on BaAl₂O₄ with

oxygenated intermediates C(O) on the soot surface was found to be the key step of soot oxidation by NO_x over BaAl₂O₄.

Spinels have also demonstrated to promote the activity of copper with regard to some other supports, such as alumina (Zawadzki et al., 2009). Copper-containing ZnAl₂O₄ spinels, with 5–12 nm size, were tested for soot combustion. An impregnated catalyst (5%CuO/ZnAl₂O₄) was more active for soot combustion than the bare support (ZnAl₂O₄), a substituted catalyst (Zn_{0.95}Cu_{0.05}Al₂O₄), and a 5%/CuO/γ-Al₂O₃ catalyst, and was similar to that of copper supported on a SrTiO₃ perovskite. The activity of 5%CuO/ZnAl₂O₄ was attributed to the easy copper reducibility.

Ceria catalysts

Cerium-based oxides are loaded on the Tree Way Catalysts used in gasoline vehicles as oxygen storage components that buffer changes in the oxidizing/reducing conditions in the exhaust gas, promote the oxidation of CO and improve the dispersion of the supported noble metals (Kaspar et al., 1999).

Ceria loaded on Diesel Particulate Filters (DPF) is also able to accelerate soot combustion and cerium additives have been used to obtain cerium-containing soot in order to promote the catalytic combustion (Lahaye1996; Makkee et al., 2002; de Sousa Filho et al., 2009).

The role of CeO₂ in the catalyzed combustion of soot has been studied (Setiabudi et al., 2004). CeO₂ has the potential to accelerate the oxidation rate of soot due to its active oxygen storage capacity. The formation of active oxygen was proposed to be initiated by NO₂ in the gas phase. A synergetic effect was observed as a result of surface nitrate decomposition, which resulted in gas phase NO₂ and desorption of active oxygen. Stored oxygen was postulated to exist in the form of surface peroxide or super oxide (Setiabudi et al., 2004). Afterwards, ESR characterization confirmed the formation of superoxide ions (O₂⁻) (Machida et al., 2008) and DRIFTS analysis confirmed the presence of both peroxide and super oxide groups on ceria surface during the catalytic combustion of soot (Gross et al., 2009; Gross et al., 2012). Active oxygen is likely to play a role on the acceleration of soot oxidation and to contribute more than desorbed NO₂ or NO₂ from surface nitrate decomposition. Isotopic experiments (Bueno-Lopez et al., 2005; Guillen Hurtado et al., 2013) have demonstrated that ceria active oxygen is able to oxidize soot directly and also via NO

386 oxidation to NO_2 , which reacts with soot afterwards, and these two reactions prevail with
387 regard to the direct oxidation of soot and NO by gas phase O_2 . On the contrary, some other
388 oxides, such as ZrO_2 or TiO_2 , for instance, have a minor or null capacity to involve catalyst
389 oxygen on the soot combustion and their catalytic activities are much lower to that of ceria
390 (Atribak et al., 2007).

391 Lahaye et al., (1996) produced soot by pyrolysis and oxidative pyrolysis of
392 hydrocarbons doped with cerium organometallic compounds, and observed that the presence
393 of cerium-based compounds had no effect on the yield or the morphology of soot but that they
394 strongly decreased the ignition temperature of the soot. It has been also reported that cerium
395 additives do not deteriorate the DPF filters while some other additives promote chemical
396 degradation (Montanaro 1999). The chemical interactions between sodium (as sulphite), iron
397 and cerium (as oxides), coming from fuel additives, and a cordierite ceramic filter were
398 studied (Montanaro 1999), and it was concluded that cerium and iron oxides do not react
399 significantly with the filter, whereas sodium leads to a diffuse etching starting from low
400 working temperatures. Several different degradation mechanisms (solid state diffusion, liquid
401 phase diffusion and evaporation–condensation) were identified as a function of the
402 temperature.

403 Different ceria-containing soot combustion catalysts have been studied as active
404 phases to be loaded on DPF filters. Harrison et al., (2003) studied ceria-supported cobalt
405 catalysts for catalytic oxidation of diesel soot with either O_2/He or $\text{NO}/\text{O}_2/\text{He}$. Co_3O_4 was
406 identified on these catalysts, and their catalytic activity was correlated with the cobalt
407 reducibility. A redox-type mechanism assisted by oxygen spillover on the CeO_2 support was
408 proposed. In contrast, cobalt supported on alumina, silica, and tin(IV) oxide showed much
409 lower activity due to the presence of dispersed Co^{2+} ions on these materials. Some of these
410 authors also proposed that the Co,Ba,K/ CeO_2 system could be a potential candidate for the
411 simultaneous abatement of soot and NO_x in diesel exhausts (Milt 2003).

412 Ceria–zirconia-supported manganese oxides (Sanchez Escribano et al., 2008) and
413 $\text{MnO}_x\text{-CeO}_2$ mixed oxides (Tikhomirov et al., 2006) have been also studied for the low-
414 temperature oxidation of diesel soot. The ignition temperature of soot for the $\text{MnO}_x\text{-CeO}_2$
415 mixed oxides was significantly lower than those for the individual oxides. This enhanced
416 activity was attributed to the improved NO_2 production. However, adding SO_2 to the model
417 gas resulted in the catalyst deactivation, which is traced to the loss of the NO oxidation

activity. The sulfates could be decomposed by heating the catalyst under reducing as well as oxidizing conditions. However, the initial activity of the catalyst could not be restored.

The promoting effect of ceria on the catalytic activity of some other phases has been also studied. V-Ce and Cu-V-Ce were tested for the oxidation of soot (Cousin et al., 2007). V-Ce oxides were active soot oxidation catalysts, and an increase in the vanadium content enhanced their catalytic activity. This was correlated with the formation of a V_2O_5 phase. However, this catalytic system (V-Ce) produced CO as soot combustion product, and adding copper to the V-Ce oxide to form a ternary system (Cu-V-Ce) had a beneficial effect on the CO_2 selectivity.

Cu-containing ceria/ceria-zirconia catalysts have been also successfully tested for soot combustion after ageing at 800°C in air (Liang et al., 2007). It was suggested that the good catalytic properties of these materials may be related to the insertion of copper into the ceria lattice and to the presence of well-dispersed CuO on ceria, which brings a strong synergistic effect between copper and cerium species. In a later study (Liang et al., 2008), the same authors prepared copper- and manganese-doped ceria catalyst, which were tested for soot combustion. The results showed that Mn^{x+} cations entered into the ceria lattice to form solid solutions, which increased the amount of oxygen vacancies and promoted surface oxygen chemisorption. Cu_xO clusters were postulated to be dispersed on the surface of ceria particles, and the interaction between copper and cerium greatly enhanced the rapid release of lattice oxygen.

Soot-combustion ceria catalysts doping with suitable cations, such as La^{3+} (Bueno-Lopez et al., 2005), Zr^{+4} (Aneggi et al., 2006; Zhu et al., 2007, Atribak et al., 2008, 2008b), Hf^{4+} (Reddy et al., 2008) and $Pr^{3+/4+}$ (Krishna et al. 2007, 2007b, 2007c), improves the features of this oxide.

$Ce_xZr_{1-x}O_2$ mixed oxides were studied for soot oxidation by NO_x/O_2 , and the catalytic activity was correlated with their NO oxidation capacity (Atribak et al., 2009). The processes occurring on the catalysts surface upon $NO + O_2$ adsorption were studied by in situ DRIFTS and a double role was attributed to the zirconium dopant. On one hand, zirconium promotes the oxidation of the adsorbed nitrogen species on the $Ce_xZr_{1-x}O_2$ surface (positive effect) but, on the other hand, it enhances the adsorption strength of the nitrogen groups and hinders NO_2 release (negative effect).

La^{3+} -doping also improved CeO_2 catalytic activity for soot oxidation with O_2 , and an optimum 5 wt. % La^{3+} -loading was obtained for catalysts calcined at 1000 °C (Bueno-Lopez

et al., 2005). This improvement was related to the increase in BET surface area and the change in the catalyst redox properties of CeO_2 brought about by doping with La^{3+} . La^{3+} decreased the onset temperature of Ce^{4+} to Ce^{3+} reduction by H_2 and increased the amount of Ce^{4+} that can be reduced by H_2 .

The effect of soot combustion ceria catalysts doping with either La^{3+} or Zr^{4+} has been recently compared (Katta 2010). It has been reported that La^{3+} promotes the creation of oxygen vacancies/defects on the ceria lattice more efficiently than Zr^{4+} , and this argument was used to explain the higher activity for soot combustion of La^{3+} doped ceria in comparison to pure ceria and Zr^{4+} -doped ceria. The catalytic activity for soot combustion of La^{3+} or $\text{Pr}^{3+/4+}$ doped cerias was also compared. $\text{Pr}^{3+/4+}$ -doping was more effective (Krishna et al. 2007, 2007b, 2007c) because these cations contribute to the redox mechanisms involved in the combustion of soot, together with the $\text{Ce}^{3+/4+}$, while La^{3+} only promotes cerium performance.

The size and structure of ceria catalysts also plays a role in soot combustion. $\text{Ce}_{0.8}\text{M}_{0.2}\text{O}_2$ ($\text{M} = \text{Sm}, \text{Zr}, \text{V}$) nanoparticles have been recently prepared and tested for soot combustion (Liu et al., 2011). The results showed that the catalysts structures depend on the different doped ions. $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$ and $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ preserved the face-centered cubic fluorite structure of CeO_2 and the nanometer size while sintered CeVO_4 crystallites were formed upon vanadium doping. Nanometer $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_2$ and $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ exhibited higher catalytic activity than conventional CeO_2 and CeVO_4 for soot combustion because their nanometer size favors a good soot-catalyst contact. In addition, ceria doping with samarium or vanadium could enhance SO_2 resistance. Ceria and ceria–zirconia catalysts have been also recently characterized and tested for soot combustion, and planes $\{100\}$ and $\{110\}$ were proposed to be more active than the $\{111\}$ facets (Aneggi et al., 2012).

Three dimensionally ordered macroporous (3DOM) $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ solid solutions have been prepared and successfully tested for diesel soot combustion (Zhang et al., 2010). It was argued that the microstructure with open, interconnected macropores of this novel catalyst facilitates the contact with soot and results in much higher catalytic activity than counterpart disordered macroporous catalysts.

Metal chlorides

Several metal chlorides were screened for the catalytic oxidation of model soot in loose contact (Mul et al., 1996). HgCl_2 , CaCl_2 , BaCl_2 , CoCl_2 , and NiCl_2 showed little activity,

484 and hydrated BiCl_3 and FeCl_3 were converted in air into BiOCl and FeOCl , which had a
485 moderate soot oxidation activity. MoCl_5 was converted into the corresponding metal oxide
486 and also showed a moderate ‘loose contact’ activity. PbCl_2 , CuCl_2 and CuCl were very active
487 catalysts, and it was suggested the in situ formation of intimate contact between the soot and
488 the metal chloride via ‘wetting’ and/or gas phase transport. However, practical application of
489 metal chlorides for the removal of soot from diesel exhaust was not recommended, because
490 they suffer from instability or high vapor pressures.

491

492

Molten salts

493

494 In 1998, Jelles et al. (1998a, 1998b; Van Setten et al., 1999b) first reported the study
495 of molten salts as diesel soot oxidation catalysts. Eutectic salt mixtures of Cs_2O , V_2O_5 and
496 MoO_3 , with a low melting point, were reported to be highly active soot combustion catalysts.
497 It was shown that some of the molten salts had a high activity above their melting point of
498 about 350 °C. Activities up to five times higher than the activity of chemically related solid
499 oxide catalysts were obtained, and this activity was observed throughout the complete
500 conversion of soot. The high activity was explained by the better contact between soot and
501 catalyst achieved by wetting of the soot by the liquid catalyst (Jelles et al., 1999).

502 Setiabudi et al. (2002) reported that molten salts are more active soot oxidation
503 catalyst than platinum for O_2 combustion, while that platinum is more active in the presence
504 of NO_x because molten salts are less active than platinum to catalyze the oxidation of NO to
505 NO_2 .

506 Open-pore ceramic foams were used as support for molten-salt diesel soot oxidation
507 catalysts (eutectic mixtures of Cs_2O , V_2O_5 , MoO_3 , and Cs_2SO_4) and the stable soot
508 combustion rates obtained were in the same order of magnitude as measured for catalytic fuel
509 additives (Van Setten et al., 1999). A molten salt ($\text{Cs}_2\text{SO}_4 \cdot \text{V}_2\text{O}_5$) based catalytic foam had an
510 onset temperature for catalytic oxidation of 320 °C (Van Setten et al., 2001b). This was a
511 promising temperature for continuous filter-regeneration applications, but the authors
512 concluded that, unfortunately, the liquid state of the catalyst made it unfit for the very
513 effective wall-flow monolith filter. They concluded that this molten salt requires a foam filter
514 as support, and also that the onset temperature of the catalytic foam of 320°C was still too
515 high to justify a change from wall-flow monolith to foam, as ceramic foam is a less effective
516 filter than the wall-flow monolith.

In another study (Van Setten et al., 2003), it was reported that the stability of the molten salt catalysts based on Cs_2O , MoO_3 , and Cs_2SO_4 , was too low for application as well. Due to partial evaporation, emission of catalyst compounds into the environment was likely and significant deactivation of the catalytic phase is unavoidable. These active phases were also found to be soluble in water, which might be disastrous in the case of condensation occurring in the exhaust pipe.

Alkali metal catalysts

Alkali metals have been studied in detail for the gasification of carbons with H_2O , CO_2 and O_2 (Gallagher & Harker, 1964; McKee, 1983; Moulijn et al., 1984) and the activity trend found for these reactions ($\text{Cs} > \text{K} > \text{Na} > \text{Li}$) is usually similar to that reported for alkali metal compounds-catalyzed diesel soot combustion (Neeft et al., 1996b).

Alkali metals have been mainly studied as promoters of some other soot combustion catalyst phases, such as ceria (Aneggi et al., 2008), spinels (CuFe_2O_4 (Shangguan et al., 1998; An et al., 2004), CoFe_2O_4 (An et al., 2004)), perovskites (LaCoO_3 (Hong et al., 1999; Wang et al., 2008), LaFeO_3 (An et al., 2004), LaCrO_3 (Russo et al., 2005), LaMnO_3 (Hong & Lee, 2006), SrTiO_3 (Białobok et al., 2007; Ura et al., 2011)), $\text{FeOx-VOy/Al}_2\text{O}_3$ (Neri et al., 2003), VOx/MO ($\text{MO}=\text{SiO}_2$, TiO_2 , ZrO_2 or Al_2O_3) (Hong & Lee, 2006; Liu et al., 2006) and $\text{Pt/Al}_2\text{O}_3$ (Krishna & Makkee, 2006) among others.

Different roles have been attributed to alkali promoters. Białobok et al., (2007) compared two groups of SrTiO_3 based perovskites prepared by alkali cations substitution in A-position (strontium) of the structure and by SrTiO_3 impregnation with the same amount of alkali metals. They observed that substituted perovskites were more active due to the changes in basicity, desorption of oxygen and surface structure. Russo et al. (2008b) also concluded that the improved activity of LaCoO_3 upon alkali doping (mainly rubidium) is due to the distortions entailed by the intrusion of the rather large rubidium ions at the lanthanum site in the LaCoO_3 perovskite lattice.

The alkali metal loading is an important issue to be taken into account. Shangguan et al. (1998) studied the promoting effect of potassium on the catalytic behavior of $\text{Cu}_{1-x}\text{K}_x\text{Fe}_2\text{O}_4$ spinels for the simultaneous removal of NO_x and diesel soot particulate and an optimum potassium loading was found for $x = 0.05$, above which the Cu-Fe active sites were covered and deactivated.

550 The combustion of soot catalyzed by alkali metals promoted $\text{FeO}_x\text{-VO}_y/\text{Al}_2\text{O}_3$ was
 551 proposed to occur through a redox mechanism, where the lattice oxygen of the active phase is
 552 involved. Iron acts favoring the oxidation–reduction process of the active vanadium phase,
 553 through the participation of the redox couple $\text{Fe(II)}\text{--}\text{Fe(III)}$, and the promoting role of
 554 alkaline dopants was attributed to the formation of low melting phase on the catalyst. The
 555 enhanced reduction of VO_x/MO ($\text{MO}=\text{SiO}_2$, TiO_2 , ZrO_2 or Al_2O_3) catalysts has been also
 556 argued to explain the promoting effect of alkali compounds (Hong & Lee, 2006; Liu et al.,
 557 2006). Unfortunately, it was concluded that, in spite of the alkali doped-vanadium oxide
 558 systems showed good activity, their practical application seems not possible due to the low
 559 thermal stability (Neri et al., 2003). Kureti et al. (2003) also reported the deactivation of a
 560 $\text{Fe}_{1.9}\text{K}_{0.1}\text{O}_3$ soot combustion catalyst, which was attributed to the agglomeration of the
 561 potassium promoter.

562 Thermal stability is one of the main drawbacks of alkali metals-containing soot
 563 combustion catalyst, not only for the mentioned vanadium formulations but for most alkali
 564 metals-containing catalysts. $\text{Pt/K-Al}_2\text{O}_3$ was studied and it was found that platinum and
 565 potassium show synergetic effect in soot combustion activity, but the active species
 566 responsible for the synergism were found to be unstable and are not regenerated (Krishna &
 567 Makkee, 2006). It has been reported the degradation of potassium catalysts due to the
 568 sublimation of potassium compounds during the soot combustion process (An & McGinn
 569 2006; López-Suárez et al., 2009; Mul et al., 1995). A Cu/K/Mo/Cl soot combustion catalyst
 570 was studied by Mul et al. (1995), and a catalytic cycle, involving Cu_2OCl_2 , was proposed to
 571 explain its high activity in loose contact with soot. However, the activity of this catalyst was
 572 only maintained as long as Cu_2OCl_2 was formed by reaction of copper molybdates with KCl ,
 573 which served as a chlorine supplier.

574 Aneggi et al., (2008) studied the catalytic oxidation of soot with alkali metals-
 575 promoted ceria and a major drawback resulted to be the loss of metal and consequent
 576 deactivation after catalysts aging, especially under water-containing atmosphere. In order to
 577 solve this problem, it has been recently reported the preparation of soot combustion catalysts
 578 consisting of alkali carbonates stabilized on aluminosilicates (Kimura et al., 2011). These
 579 novel catalysts were prepared by ion exchange of alkali compounds on zeolites, which were
 580 finally collapsed at high temperature, and it was reported that they overcome the drawback of
 581 the high solubility of alkali compounds on water.

582 Several authors have observed that transition elements can moderate the loss of
583 potassium (An & McGinn 2006). The stability of potassium in soot combustion copper-
584 containing SrTiO_3 perovskite catalysts has been studied (López Suárez 2009), concluding that
585 the synthesis method used for potassium addition (impregnation or substitution into the
586 lattice) affects notably the catalysts stability, and that the substituted catalysts were more
587 stable due to the location of potassium inside the perovskite structure.

588 In spite of the attempts to prepare stable alkali metal-containing soot combustion
589 catalysts, the hydrothermal stability seems to be still a major problem to be solved for a
590 practical use of alkali metals on soot combustion catalysts formulations.

591

592 Conclusions

593

594 The most relevant information available about the different active phases that have
595 been studied for the catalytic combustion of soot has been reviewed and discussed in this
596 article. Many catalysts have been reported to accelerate soot combustion, including
597 formulations with noble metals, alkali and alkali earth metals, transition metals that can
598 accomplish redox cycles (V, Mn, Co, Cu, Fe...) and internal transition metals.

599 Platinum catalysts are among the most interesting for practical application. The main
600 role of platinum is to promote NO oxidation to NO_2 , and one important feature of these
601 catalysts is that sulfur resistant platinum formulations have been prepared.

602 Some metal oxide-based catalysts seem also promising candidates for soot combustion
603 in practical applications, including ceria-based formulations and mixed oxides with
604 perovskite and spinel structure. In addition to catalyze the oxidation of NO to NO_2 , some of
605 these metal oxide catalysts also produce highly reactive active oxygen species. In this case,
606 the catalyst must be loaded into the DPF filter and dual bed configurations (for instance, DOC
607 + DPF such as in the CRT system) are not suitable.

608 Thermal stability is one important requirement for a soot combustion catalyst, and this
609 rules out the practical utilization of several potential catalysts like most alkali metal catalysts,
610 molten salts and metal chlorides. Some noble metal catalysts are also unstable because they
611 form volatile oxides (ruthenium, iridium and osmium).

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