Diesel soot combustion catalysts: a review of active phases.

Ana M. Hernández-Giménez, Dolores Lozano Castelló, Agustín Bueno-López*.

Department of Inorganic Chemistry, University of Alicante,

Corresponding author: Agustín Bueno López, agus@ua.es; Ap.99, E-03080 Alicante (Spain).

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).

Introduction

Soot particles are emitted by Diesel engines together with NOx, CO and unburned hydrocarbons (HC) in gas streams with high O_2, CO_2 and H_2O concentrations and temperatures typically below 500-550 ºC. In these conditions, CO and HC oxidation can be easily accomplished in a Diesel Oxidation Catalyst (DOC), but both NOx 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 NO_2. NO_2 is much more oxidizing than NO and O_2 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 NOx Reduction) system for the simultaneous removal of NOx 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.

In addition to these particular features of the soot combustion reactions, the reaction rate also depends on general variables, such as, temperature for isothermal reactions and heating rate for ramp experiments, nature and partial pressure of the gases in the stream, space velocity/residence time of the gases in the solid bed, soot/catalyst ratio, etc. In order to restrict the information spread on literature to results with a certain practical relevance, only data obtained with catalysts tested in "loose contact" with soot and under both NOx and O_2 containing gas mixtures have been considered in Table 1. However, in spite of these precautions, it is not possible to achieve realistic conclusions about which catalyst is best and which one is worst from data included in Table 1, and it is not the intention of this review article to do it. The aim of the article is to compile the tremendous information available on literature and to critically discuss this information identifying strong and weak points of each type of catalyst.

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

Table 1. Compilation of soot combustion catalytic tests results. Only catalysts tested in "loose contact" with soot and under both NOx and O_2 containing gas mixtures have been considered; only results obtained with fresh catalysts are included.

119

Catalysts	ΔT	T_{max}	Relevant experimental details	Reference
SiO_2		661		
$1\%Pt/SiO_2$		312	500 ml/min; 10% O_2 +7% H_2O + 1000 ppm NO + 100 ppm SO_2 in N_2; Flow reactor; 10 ℃/min;	Oi-Uchisawa et a.,
$1\%Pt/Al_2O_3$		460	5 mg of soot + 500 mg catalyst; carbon black (Nippon Tokai carbon 7350F)	1998
$1\%Pt/ZrO_2$		408		
SiO_2		687		
$1\%Pt/SiO_2$		562		
V_2O_5/SiO_2		555	500 ml/min; 1000 ppm NO +10% O_2 + 7% H_2O in N_2; Flow reactor; 10 ℃/min; 5 mg of soot +	Liu et al., 2001
V_2O_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_2O_3 (260 m^2/g)		~650		
$1\%Pt/\gamma$-Al_2O_3 (210 m^2/g)		~550	100 ml/min; 2000 ppm NOx + 5% O_2 in He; Flow reactor; 15 ℃/min; 66 mg (1:9 soot:catalyst);	Castoldi et al., 2006
$1\%Pt/20\%Ba/\gamma$-Al_2O_3 (160 m^2/g)		~580	Printex U.	
$2.5\%Pt/4\%K_2O/Al_2O_3$	150	375	200 ml/min; 600 ppm NOx + 10% O_2 in Ar; Flow reactor; 1 ℃/min; 100 mg (1:4 soot:catalyst); 43000 h^{-1}; Printex U.	Krishna & Makkee, 2006
Cs_2SO_4·V_2O_5/foam filter		~475	200 ml/min; 600 ppm NOx + 10% O_2 in Ar; Flow reactor; 0.6 ℃/min Printex U.	Setiabudi et al.,
$1\%Pt/Al_2O_3$		~415		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 ℃/min; 10 mg of soot + 100 mg catalyst; Printex U.	Wei et al., 2013
$8\%Pt/Ce_{0.8}Zr_{0.2}O_2$ (3DOM)	259	326		
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 NOx + 5% O_2 in N_2. Flow reactor; 10 ℃/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 NOx + 5% O_2 in He; Flow reactor; 1 ℃/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_2O in N_2. Flow reactor; 10 ℃/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		
$Ce_{0.9}La_{0.1}O_x$ (16 m^2/g)	68	460		
$Ce_{0.9}Pr_{0.1}O_x$ (11 m^2/g)	109	419	200 ml/min; 600 ppm NOx + 10% O_2 in Ar; Flow reactor; 0.6 ºC/min;	Krishna et al.,
$Ce_{0.9}Sm_{0.1}O_x$ (5 m^2/g)	35	493	100 mg (1:4 soot:catalyst); 70000 h^{-1}; Printex U.	2007b
$Ce_{0.9}Y_{0.1}O_x$ (2 m^2/g)	24	504		
Pt/Al_2O_3 (comercial)		~515		
CeO_2 (37 m^2/g)		~550		
$Mn_{0.25}Ce_{0.75}O_x$ (86 m^2/g)		~460	140 ml/min; 10% O_2 + 1000 ppm NO + 3% H_2O in N_2; TGA reactor; 10 ºC/min; 5 mg of soot +	Tikhomirov et al.,
$Mn_{0.50}Ce_{0.50}O_x$ (79 m^2/g)		~590	100 mg catalyst; Real soot.	2006
$Mn_{0.75}Ce_{0.25}O_x$ (89 m^2/g)		~500		
Mn_2O_3 (24 m^2/g)		~585		
CeO_2 (62 m^2/g)		~465		
$CuO-CeO_2$ (68 m^2/g)		~420	500 ml/min; 1000 ppm NO + 9.5% O_2 in N_2; Flow reactor; 20 ºC/min; 5 mg of soot + 100 mg	Wu et al., 2007
CeO_2-ZrO_2 (57 m^2/g)		~478	catalyst; Printex U.	
$CuO-CeO_2-ZrO_2$ (51 m^2/g)		~448		
La_2CuO_4		504		
Pr_2CuO_4		507		
Nd_2CuO_4		518	50 ml/min; 2000 ppm NO+ 5% O_2 in He; Flow reactor; 2 ºC/min; 108 mg (1:5 soot:catalyst)	Liu et al., 2008
Sm_2CuO_4		518	Flow reactor; Printex U.	
Gd_2CuO_4		520		
$La_{1.3}Na_{0.7}CuO_4$		463		
$ZnAl_2O_4$ (133 m^2/g)	35	630	500 ml/min; 500 ppm NOx + 5% O_2 in N_2; Flow reactor; 10 ºC/min; 100 mg (1:4 soot:catalyst);	Zawadzki et al.,
5%$CuO/ZnAl_2O_4$ (111 m^2/g)	65	600	30000 h^{-1}; carbon black (Vulcan XC72)	2009
$Zn_{0.95}Cu_{0.05}Al_2O_4$ (148 m^2/g)	18	647		
$K-Cu/SrTiO_3$ (9 m^2/g)	188	495		
$Sr_{0.8}K_{0.2}TiO_x$ (5 m^2/g)	215	468	500 ml/min; 500 ppm NOx + 5% O_2 in N_2; Flow reactor; 10 ºC/min; 100 mg (1:4 soot:catalyst);	López-Suárez et
$K/SrTiO_3$ (7 m^2/g)	195	488	30000 h^{-1}; carbon black (Vulcan XC72)	al., 2009
$Cu/SrTiO_3$ (11 m^2/g)	78	605		
$LaCoO_3$ (9 m^2/g)	178	421	50 ml/min; 2000 ppm NOx + 5% O_2 in He; Flow reactor; 2 ºC/min; 180 mg (1:5 soot:catalyst)	Wang et al., 2008
$La_{0.90}K_{0.10}CoO_3$ (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 ºC/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 ºC/min; Printex U.	Zheng et al., 2012

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

121 T_{max}: Temperature of maximum soot combustion rate, maximum COx emission or temperature for 50% soot conversion (ºC).

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 NO_2 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 O_2 has been postulated to be the spillover of activated oxygen (Neri et al., 1997) and, on NOx/O_2 mixtures, the catalytic oxidation of NO to NO_2 (Setiabudi et al., 2002). In presence of both NO_2 and O_2, it has been also reported (Jeguirim et al., 2007) that besides the well-established catalytic oxidation of NO into NO_2, Pt also has a catalytic effect on the cooperative carbon–NO_2–O_2 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 NO_2 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 N_2, O_2, H_2O, NO and SO_2 (Oi-Uchisawa et al., 1998). The platinum precursors compared were $Pt(NH_3)_4(OH)_2$, $H_2PtCl_6 \cdot 6H_2O$, $Pt(NH_3)_4(NO_3)_2$, and $Pt(NH_3)_4Cl_2$ and the supports tested were SiO_2, Al_2O_3, and ZrO_2. Pt/SiO_2 prepared from $Pt(NH_3)_4(OH)_2$ 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 NO_2. 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 (Ta_2O_5, Nb_2O_5, WO_3, SnO_2, SiO_2, TiO_2, Al_2O_3 and ZrO_2). Pt/Ta_2O_5 showed the highest activity in a model diesel exhaust containing O_2, H_2O, NO and SO_2 in N_2. Platinum catalysts supported on other non-basic metal oxides such as Nb_2O_5, WO_3, SnO_2 and SiO_2 showed similar high activities. The high activity for these catalysts was attributed to their non-basicity and negligible affinity toward SO_3 (or H_2SO_4), which resulted in less poisoning of the supported platinum. The MOx supports used for platinum catalysts were further improved by using MOx-TiO_2 mixtures (Oi-Uchisawa et al., 2003), and highest activities

were obtained with $Pt/(TiO_2+SiO_2)$ for molar ratios of $TiO_2/(TiO_2+SiO_2)$ 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 SiO_2-supported MoO_3, V_2O_5, 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 O_2 to NO_2, while MoO_3 and V_2O_5 catalyze the oxidation of carbon with NO_2. 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 NO_2, which subsequently oxidizes soot using cerium as a catalyst, forming NO which can participate in the reaction more than once.

Recently, three-Dimensional Ordered Macroporous (3DOM) $Ce_{0.8}Zr_{0.2}O_2$-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 $Pt/Ce_{0.8}Zr_{0.2}O_2$ 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 NOx storage capacity of $Pt–Mg/Al_2O_3$ catalyst. More NO_2 is produced in the temperature range of soot oxidation on $Pt–Mg/Al_2O_3$ than on a Mg-free Pt/Al_2O_3 catalyst with a similar Pt particle size, which efficiently promotes the ignition of soot.

Soot combustion on NSR (NOx 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 NOx and soot (DPNR systems; Diesel Particulate NOx 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 O_2-righ and O_2-lean atmospheres. NOx are chemisorbed on the basic compounds during the O_2-rich cycles and are reduced during the lean periods attained by extra diesel injection.

188 The potential utilization of a typical Pt–Ba/Al$_2$O$_3$ NSR catalyst for the simultaneous
189 removal of soot and NOx was investigated and compared with that of a Pt/Al$_2$O$_3$ sample
190 (Castoldi et al., 2006). It was found that the Pt–Ba/Al$_2$O$_3$ catalyst was able to simultaneously
191 remove both soot and NOx while the Pt/Al$_2$O$_3$ catalyst effectively performed the soot
192 oxidation but was not able to remove gas phase NOx to a significant extent. These authors
193 observed that the presence of soot did not significantly affect NOx reduction on the Pt–
194 Ba/Al$_2$O$_3$ catalyst (Castoldi et al., 2006). On the contrary, Klein et al. (2012) also studied the
195 effect of soot on the performance of PtBa/Al$_2$O$_3$ NSR catalysts and reported that the presence
196 of soot in the catalytic bed leads to the decrease of the NOx storage capacity (NSC) of the
197 catalysts. Participation of a direct reaction between carbon particles and NOx 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 NOx
205 storage capacity (Klein et al., 2013).

206 Soot oxidation activity and deactivation of NSR catalysts containing Pt, K, and Ba
207 supported on Al$_2$O$_3$ 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 NO$_2$ followed by NO recycle to NO$_2$, and soot oxidation
210 with O$_2$ assisted by NO$_2$. Only a part of the stored NOx that was decomposed at high
211 temperatures under lean conditions was found to be useful for soot oxidation. NOx storage
212 capacity of these NSR catalysts decreased upon aging under soot oxidizing conditions. Pt/K–
213 Al$_2$O$_3$ catalyst was more active, but least stable compared with Pt/Ba–Al$_2$O$_3$ because the
214 active species responsible for synergism on Pt/K–Al$_2$O$_3$ 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–Al$_2$O$_3$ 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 NOx species and is
219 not promoted by platinum. This surface reaction mechanism parallels the gas-phase soot
220 oxidation by NO$_2$ and O$_2$ evolved upon decomposition of the stored NOx. Potassium-based

221 catalysts are more active than Ba-containing catalysts due to the higher mobility of the NOx

222 species adsorbed on potassium with respect to barium.

223

224 **Non-platinum noble metals and silver catalysts**

225

226 Non-platinum noble metals have not been studied very often as soot combustion

227 catalyst, and few articles have been reported regarding the study of silver catalysts.

228 Na-Y zeolite-supported iridium, palladium, platinum, and rhodium metals were

229 screened as carbon oxidation catalysts, and ruthenium was proposed to be the most active

230 noble metal (Villani et al., 2006). However, it is known that ruthenium (and also iridium and

231 Osmium) form volatile oxides, which rules out its practical utilization (Gandhi et al., 2003).

232 Au–V-based catalysts have been studied for soot combustion with special attention to

233 the reaction mechanism (Van Craenenbroeck et al., 2002). Gold particles do provide very

234 active sites able to ignite soot within the desired temperature range but retard the oxidation

235 process at high vanadium loadings because of the diminished contact. Gold particles were

236 proposed to promote the oxygen transfer from catalyst to soot, which increases the activity in

237 the combustion of soot particles. This positive effect could become negative because the same

238 oxygen donor property might be responsible for the formation of polyvanadate clusters

239 instead of V_2O_5 crystallites, diminishing the mobility of the catalyst.

240 The effect of 2% gold addition to $LaBO_3$ perovskite catalysts (B = Cr, Mn, Fe and Ni)

241 was also studied in the simultaneous CO and soot combustion (Russo et al., 2008). The

242 comparison of their activity with those of the corresponding gold-free pure perovskite

243 evidenced that the presence of gold had a good synergetic effect towards CO oxidation and a

244 negligible one towards carbon combustion.

245 Soot combustion over silver-supported catalysts was studied by using Al_2O_3, CeO_2

246 and ZrO_2 supports (Aneggi et al., 2009). Formation of Ag/Ag_2O mixtures was observed in all

247 supports and their relative abundance is strictly correlated to the nature of the support. Ceria

248 was shown to stabilize silver oxide while with ZrO_2 and Al_2O_3 metallic silver was

249 preferentially formed. For this reason, it was proposed that Ag/ZrO_2 and Ag/Al_2O_3 were

250 active catalysts while the bare ZrO_2 and Al_2O_3 supports were not. On the contrary, silver

251 addition to ceria had little benefit, because ceria itself is active in soot oxidation and silver

252 forms a low active oxide. However, it has been recently reported the preparation of very

253 active Ag/CeO_2 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

ABO_3 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 NOx and diesel soot in the presence of oxygen, and were superior to transition metal simple oxides in the selectivity for NOx 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. $La_{1-x}K_xMnO_3$ perovskite catalysts were also tested for the simultaneous removal of NOx 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 NOx reduction selectivity for N_2 depended significantly on the potassium content, being highest for compositions close to the solubility limit. ABO_3 perovskites with A= La+K and B = Cu+V were also effective for the simultaneous removal of soot and NOx at 450–500 °C, but the stability at high temperature (800 °C) was poor (Fino et al., 2003).

$LaCrO_3$, $LaFeO_3$ and $LaMnO_3$ 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 300–500ºC (Fino et al., 2003b). Lithium introduction on chromium position of $LaCrO_3$ 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 $LaMnO_3$ 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 $LaCoO_3$.

Hirano et al., (2009) studied strontium-substituted $LaFeO_3$ perovskites for soot combustion, and the activity of these perovskites was reported to be only slightly lower to that of a Pt/Al_2O_3 reference catalyst. Teraoka et al., (1996) also reported that Co, Mn and Fe perovskite-type and Cu-based K_2NiF_4-type oxides (all with La^{3+} partially substituted by alkali or alkali metal cations) catalyze the simultaneous removal of NOx and diesel soot particulate

287 and that these perovskite related oxides are superior to transition metal simple oxides and

288 Pt/Al$_2$O$_3$ with respect to the selectivity to NOx reduction.

289 SrTiO$_3$ 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 SrTiO$_3$ < Li/SrTiO$_3$ < Cs/SrTiO$_3$ < K/SrTiO$_3$. 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 NOx/O$_2$ of potassium

294 impregnated and substituted SrTiO$_3$ 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 SrTiO$_3$ perovskite activity for the

298 catalytic combustion of soot has been also reported. The higher activity of Cu/SrTiO$_3$ in

299 comparison to Cu/Al$_2$O$_3$ was attributed to the improved redox properties of copper originated

300 by Cu-support interactions, which improve the catalytic oxidation of NO to NO$_2$. This seems

301 to be related to the presence of weakly bound oxygen on this sample, since copper species

302 present on the Cu/SrTiO$_3$ 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$_x$Fe$_{1-x}$O$_3$, Zhang et al. (2010b) prepared La$_{0.9}$K$_{0.1}$CoO$_3$ and

307 Zheng et. al. (2012) prepared LaMn$_{1-x}$Fe$_x$O$_3$.

308 Several perovskite catalysts have been coated on particulate filters and the

309 regeneration has been evaluated. The PrCrO$_3$ perovskite supported on CeO$_2$ 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/Al$_2$O$_3$ catalysts.

313 The La$_{0.8}$Ce$_{0.2}$MnO$_3$ 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$_{0.2}$MnO$_3$ perovskite was fully microwave –assisted

319 regenerated with almost 100% selectivity towards CO$_2$. In contrast, the same filter without

320 such a coating was only partially regenerated, and considerable amounts of CO were formed.
321 The $La_{0.8}Ce_{0.2}MnO_3$ coating showed excellent temperature shock resistance and thermo-
322 chemical stability and the authors proposed that, once a suitable microwave cavity is
323 designed, microwave assisted soot filter regeneration would be feasible.

324 However, formation of perovskite structures not always has a positive effect on the
325 soot combustion activity of mixed oxides, and few examples of catalyst deactivation due to
326 perovskite structure formation have been reported. The stability of $Ba,K/CeO_2$ catalysts,
327 which have been shown to be very active for soot combustion, was studied and , above 830ºC,
328 catalyst deactivation due to $BaCeO_3$ perovskite structure formation was observed (Peralta et
329 al., 2006).

Spinel catalysts

332 Shangguan et al. (1996) studied the simultaneous removal of NOx and diesel soot
333 particulate in the presence of excess oxygen with ternary AB_2O_4 spine1 oxides. The catalytic
334 performance depended significantly on the metal cations used, and $CuFe_2O_4$ was the best
335 catalyst. The performance of this spinel catalyst was much better than that of the mechanical
336 mixtures of the metal oxides. This conclusion was also extended to Cu-Cr systems.

337 Nanostructured spinel-type oxide catalysts AB_2O_4 (where A = Co and Mn, and B = Cr
338 and Fe) have also demonstrated to be effective for the simultaneous removal of soot and NOx
339 (Fino et al., 2006). The activity order for soot combustion was found to be $CoCr_2O_4$ >
340 $MnCr_2O_4$ > $CoFe_2O_4$, whereas the activity order for NOx reduction was $CoFe_2O_4$ > $CoCr_2O_4$
341 > $MnCr_2O_4$. The best compromise between simultaneous abatement of soot and nitrogen
342 oxide was therefore shown by the $CoCr_2O_4$ catalyst, which could promote soot combustion
343 and appreciable NOx reduction below 400 ºC. The prevalent catalytic combustion activity of
344 the chromite catalysts could be explained by their higher concentration of suprafacial, weakly
345 chemisorbed oxygen, which contributes actively to soot combustion by spillover. A $CoAl_2O_4$
346 spinel catalyst has also shown an activity for soot combustion reaction similar to that of a
347 Pt/Al_2O_3 reference catalyst (Zawadzki et al., 2011). This high soot combustion activity of
348 $CoAl_2O_4$ was attributed to its high NOx chemisorption capacity, what allowed fast NO
349 oxidation to NO_2.

350 $BaAl_2O_4$ spinel was also proved to be an effective to catalyze the reaction between
351 soot and NOx under lean-burn condition, promoting the simultaneous NOx reduction to N_2
352 and soot oxidation to CO_2 (Lin et al., 2009). The interaction of nitrates on $BaAl_2O_4$ with

353 oxygenated intermediates C(O) on the soot surface was found to be the key step of soot

354 oxidation by NOx over $BaAl_2O_4$.

355 Spinels have also demonstrated to promote the activity of copper with regard to some

356 other supports, such as alumina (Zawadzki et al., 2009). Copper-containing $ZnAl_2O_4$ spinels,

357 with 5–12 nm size, were tested for soot combustion. An impregnated catalyst

358 ($5\%CuO/ZnAl_2O_4$) was more active for soot combustion than the bare support ($ZnAl_2O_4$), a

359 substituted catalyst ($Zn_{0.95}Cu_{0.05}Al_2O_4$), and a $5\%/CuO/\gamma$-Al_2O_3 catalyst, and was similar to

360 that of copper supported on a $SrTiO_3$ perovskite. The activity of $5\%CuO/ZnAl_2O_4$ was

361 attributed to the easy copper reducibility.

362

363 **Ceria catalysts**

364

365 Cerium-based oxides are loaded on the Tree Way Catalysts used in gasoline vehicles

366 as oxygen storage components that buffer changes in the oxidizing/reducing conditions in the

367 exhaust gas, promote the oxidation of CO and improve the dispersion of the supported noble

368 metals (Kaspar et al., 1999).

369 Ceria loaded on Diesel Particulate Filters (DPF) is also able to accelerate soot

370 combustion and cerium additives have been used to obtain cerium-containing soot in order to

371 promote the catalytic combustion (Lahaye1996; Makkee et al., 2002; de Sousa Filho et al.,

372 2009).

373 The role of CeO_2 in the catalyzed combustion of soot has been studied (Setiabudi et

374 al., 2004). CeO_2 has the potential to accelerate the oxidation rate of soot due to its active

375 oxygen storage capacity. The formation of active oxygen was proposed to be initiated by NO_2

376 in the gas phase. A synergetic effect was observed as a result of surface nitrate

377 decomposition, which resulted in gas phase NO_2 and desorption of active oxygen. Stored

378 oxygen was postulated to exist in the form of surface peroxide or super oxide (Setiabudi et al.,

379 2004). Afterwards, ESR characterization confirmed the formation of superoxide ions (O_2^-)

380 (Machida et al., 2008) and DRIFTS analysis confirmed the presence of both peroxide and

381 super oxide groups on ceria surface during the catalytic combustion of soot (Gross et al.,

382 2009; Gross et al., 2012). Active oxygen is likely to play a role on the acceleration of soot

383 oxidation and to contribute more than desorbed NO_2 or NO_2 from surface nitrate

384 decomposition. Isotopic experiments (Bueno-Lopez et al., 2005; Guillen Hurtado et al., 2013)

385 have demonstrated that ceria active oxygen is able to oxidize soot directly and also via NO

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

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

Different ceria-containing soot combustion catalysts have been studied as active phases to be loaded on DPF filters. Harrison et al., (2003) studied ceria-supported cobalt catalysts for catalytic oxidation of diesel soot with either O_2/He or NO/O_2He. Co_3O_4 was identified on these catalysts, and their catalytic activity was correlated with the cobalt reducibility. A redox-type mechanism assisted by oxygen spillover on the CeO_2 support was proposed. In contrast, cobalt supported on alumina, silica, and tin(IV) oxide showed much lower activity due to the presence of dispersed Co^{2+} ions on these materials. Some of these authors also proposed that the $Co,Ba,K/CeO_2$ system could be a potential candidate for the simultaneous abatement of soot and NOx in diesel exhausts (Milt 2003).

Ceria–zirconia-supported manganese oxides (Sanchez Escribano et al., 2008) and MnOx-CeO_2 mixed oxides (Tikhomirov et al., 2006) have been also studied for the low-temperature oxidation of diesel soot. The ignition temperature of soot for the MnOx-CeO_2 mixed oxides was significantly lower than those for the individual oxides. This enhanced activity was attributed to the improved NO_2 production. However, adding SO_2 to the model 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 800ºC 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 NOx/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 ºC (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 $Pr^{3+/4+}$ doped cerias was also compared. $Pr^{3+/4+}$-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 $Ce^{3+/4+}$, while La^{3+} only promotes cerium performance.

The size and structure of ceria catalysts also plays a role in soot combustion. $Ce_{0.8}M_{0.2}O_2$ (M = Sm, Zr, 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. $Ce_{0.8}Sm_{0.2}O_2$ and $Ce_{0.8}Zr_{0.2}O_2$ 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 $Ce_{0.8}Sm_{0.2}O_2$ and $Ce_{0.8}Zr_{0.2}O_2$ 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) $Ce_{1-x}Zr_xO_2$ 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,

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

Molten salts

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

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

Open-pore ceramic foams were used as support for molten-salt diesel soot oxidation catalysts (eutectic mixtures of Cs_2O, V_2O_5, MoO_3, and Cs_2SO_4) and the stable soot combustion rates obtained were in the same order of magnitude as measured for catalytic fuel additives (Van Setten et al., 1999). A molten salt ($Cs_2SO_4 \cdot V_2O_5$) based catalytic foam had an onset temperature for catalytic oxidation of 320 °C (Van Setten et al., 2001b). This was a promising temperature for continuous filter-regeneration applications, but the authors concluded that, unfortunately, the liquid state of the catalyst made it unfit for the very effective wall-flow monolith filter. They concluded that this molten salt requires a foam filter as support, and also that the onset temperature of the catalytic foam of 320°C was still too high to justify a change from wall-flow monolith to foam, as ceramic foam is a less effective 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 (Cs > K > Na > 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)), $FeOx-VOy/Al_2O_3$ (Neri et al,. 2003), VOx/MO ($MO=SiO_2$, TiO_2, ZrO_2 or Al_2O_3) (Hong & Lee, 2006; Liu et al., 2006) and Pt/Al_2O_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 (stromtium) 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 $Cu_{1-x}K_xFe_2O_4$ spinels for the simultaneous removal of NOx and diesel soot particulate and an optimum potassium loading was found for for x = 0.05, above which the Cu-Fe active sites were covered and deactivated.

The combustion of soot catalyzed by alkali metals promoted FeOx-VOy/Al_2O_3 was proposed to occur through a redox mechanism, where the lattice oxygen of the active phase is involved. Iron acts favoring the oxidation–reduction process of the active vanadium phase, through the participation of the redox couple Fe(II)–Fe(III), and the promoting role of alkaline dopants was attributed to the formation of low melting phase on the catalyst. The enhanced reduction of VO_x/MO (MO=SiO_2, TiO_2, ZrO_2 or Al_2O_3) catalysts has been also argued to explain the promoting effect of alkali compounds (Hong & Lee, 2006; Liu et al., 2006). Unfortunately, it was concluded that, in spite of the alkali doped-vanadium oxide systems showed good activity, their practical application seems not possible due to the low thermal stability (Neri et al., 2003). Kureti et al. (2003) also reported the deactivation of a $Fe_{1.9}K0_{.1}O_3$ soot combustion catalyst, which was attributed to the agglomeration of the potassium promoter.

Thermal stability is one of the main drawbacks of alkali metals-containing soot combustion catalyst, not only for the mentioned vanadium formulations but for most alkali metals-containing catalysts. Pt/K–Al_2O_3 was studied and it was found that platinum and potassium show synergetic effect in soot combustion activity, but the active species responsible for the synergism were found to be unstable and are not regenerated (Krishna & Makkee, 2006). It has been reported the degradation of potassium catalysts due to the sublimation of potassium compounds during the soot combustion process (An & McGinn 2006; López-Suárez et al., 2009; Mul et al., 1995). A Cu/K/Mo/Cl soot combustion catalyst was studied by Mul et al. (1995), and a catalytic cycle, involving Cu_2OCl_2, was proposed to explain its high activity in loose contact with soot. However, the activity of this catalyst was only maintained as long as Cu_2OCl_2 was formed by reaction of copper molybdates with KCl, which served as a chlorine supplier.

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

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

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

Conclusions

The most relevant information available 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. The main role of platinum is to promote NO oxidation to NO_2, 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 structure. In addition to catalyze the oxidation of NO to NO_2, some of these metal oxide catalysts also produce highly reactive active oxygen species. In this case, the catalyst must be loaded into the DPF filter and dual bed configurations (for instance, DOC + DPF such as in the CRT system) are not suitable.

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).

References

An, H., Kilroy, C., & McGinn P. J. (2004). *Combinatorial synthesis and characterization of alkali metal doped oxides for diesel soot combustion. Catalysis Today 98,* 423–429. doi:10.1016/j.cattod.2004.08.006.

An, H. & McGinn, P.J. (2006). *Catalytic behavior of potassium containing compounds for diesel soot combustion. Applied Catalysis B-Environmental 62,* 46–56. doi:10.1016/j.apcatb.2005.06.013.

Aneggi, E., de Leitenburg, C., Dolcetti, G. & Trovarelli, A. (2006). *Promotional effect of rare earths and transition metals in the combustion of diesel soot over CeO_2 and CeO_2-ZrO_2. Catalysis Today 114* (1), 40-47. doi:10.1016/j.cattod.2006.02.008.

Aneggi, E., de Leitenburg, C., Dolcetti, G. & Trovarelli, A. (2008). *Diesel soot combustion activity of ceria promoted with alkali metals. Catalysis Today 136* (2008) 3–10. doi:10.1016/j.cattod.2008.01.002.

Aneggi, E., Llorca, J., de Leitenburg, C., Dolcetti, G. & Trovarelli, A. (2009). *Soot combustion over silver-supported catalysts. Applied Catalysis B-Environmental 91* (1-2), 489-498. doi:10.1016/j.apcatb.2009.06.019.

Aneggi, E., de Leitenburg, C., Llorca, J. & Trovarelli, A. (2012). *Higher activity of Diesel soot oxidation over polycrystalline ceria and ceria-zirconia solid solutions from more reactive surface planes. Catalysis Today 197* (1), 119-126. http://dx.doi.org/10.1016/j.cattod.2012.07.030.

Atribak, I., Such-Basáñez, I., Bueno-López, A. & García, A. (2007). *Comparison of the catalytic activity of MO_2 (M = Ti, Zr, Ce) for soot oxidation under NOx/O_2. Journal of Catalysis 250* (1), 75-84. doi:10.1016/j.jcat.2007.05.015.

Atribak, I., Bueno-López, A. & García-García, A. (2008). *Thermally stable ceria-zirconia catalysts for soot oxidation by O_2. Catalysis Communications 9* (2), 250-255. doi:10.1016/j.catcom.2007.05.047.

Atribak, I., Bueno-López, A. & García-García, A. (2008b). *Combined removal of diesel soot particulates and NO x over CeO₂-ZrO₂ mixed oxides. Journal of Catalysis 259* (1), 123-132. doi:10.1016/j.jcat.2008.07.016.

Atribak, I., Azambre, B., Bueno López, A. & García-García, A. (2009). *Effect of NOx adsorption/desorption over ceria-zirconia catalysts on the catalytic combustion of model soot. Applied Catalysis B-Environmental 92* (1-2), 126-137. doi:10.1016/j.apcatb.2009.07.015.

Białobok, B., Trawczyński, J., Rzadki, T., Miśta, W. & Zawadzki, M. (2007). *Catalytic combustion of soot over alkali doped SrTiO₃. Catalysis Today 119* (1-4), 278-285. doi:10.1016/j.cattod.2006.08.024.

Bueno-López, A., Krishna, K., Makkee, M. & Moulijn, J.A. (2005). *Enhanced soot oxidation by lattice oxygen via La³⁺-doped CeO₂. Journal of Catalysis 230* (1), 237-248. doi:10.1016/j.jcat.2004.11.027.

Castoldi, L., Matarrese, R., Lietti, L. & Forzatti, P. (2006). *Simultaneous removal of NOx and soot on Pt–Ba/Al₂O₃ NSR catalysts. Applied Catalysis B-Environmental 64*, 25–34. doi:10.1016/j.apcatb.2005.10.015.

Cousin, R., Capelle, S., Abi-Aad, E., Courcot, D. & Aboukaïs, A. (2007). *Copper-vanadium-cerium oxide catalysts for carbon black oxidation. Applied Catalysis B-Environmental 70* (1-4), 247-253. doi:10.1016/j.apcatb.2006.01.019.

de Sousa Filho, P. C., Gomes, L.F., de Oliveira, K.T., Neri, C.R. & Serra, O.A. (2009). *Amphiphilic cerium(III) β-diketonate as a catalyst for reducing diesel/biodiesel soot emissions. Applied Catalysis A-General 360* (2), 210-217. doi:10.1016/j.apcata.2009.03.024.

Fino, D., Fino, P., Saracco, G. & Specchia, V. (2003). *Studies on kinetics and reactions mechanism of La₂₋ₓKₓCu₁₋ᵧVᵧO₄ layered perovskites for the combined removal of diesel particulate and NOx. Applied Catalysis B-Environmental 43* (3), 243-259. doi:10.1016/S0926-3373(02)00311-9.

Fino, D., Russo, N., Saracco, G. & Specchia, V. (2003b). *The role of suprafacial oxygen in some perovskites for the catalytic combustion of soot. Journal of Catalysis 217* (2), 367-375. doi:10.1016/S0021-9517(03)00143-X.

Fino, D. & Specchia, V. (2004). *Compositional and structural optimal design of a nanostructured diesel-soot combustion catalyst for a fast-regenerating trap. Chemical Engineering Science 59* (22-23), 4825-4831. doi:10.1016/j.ces.2004.07.012.

677 Fino, D., Russo, N., Saracco, G. & Specchia, V. (2006). *Catalytic removal of NOx and diesel*
678 *soot over nanostructured spinel-type oxides. Journal of Catalysis 242* (1), 38-47.
679 doi:10.1016/j.jcat.2006.05.023.

680 Fino, D., Russo, N., Cauda, E., Saracco, G. & Specchia, V. (2006b). *La-Li-Cr perovskite*
681 *catalysts for diesel particulate combustion. Catalysis Today 114* (1), 31-39.
682 doi:10.1016/j.cattod.2006.02.007.

683 Fino, D. & Specchia, V. (2008). *Open issues in oxidative catalysis for diesel particulate*
684 *abatement. Powder Technology 180*, 64-73. doi:10.1016/j.powtec.2007.03.021.

685 Gallagher J.T. & Harker H. (1964). *Reaction of carbon with oxidizing gases: Catalysis by*
686 *compounds of iron, cobalt and nickel. Carbon. 2*, 163-174. http://dx.doi.org/10.1016/0008-
687 6223(64)90057-0.

688 Gandhi, H.S., Graham, G.W. & McCabe, R.W. (2003). *Automotive exhaust catalysis. Journal*
689 *of Catalysis 216*, 433–442. doi:10.1016/S0021-9517(02)00067-2.

690 Gross, M.S., Ulla, M.A. & Querini, C.A. (2009). *Catalytic oxidation of diesel soot: New*
691 *characterization and kinetic evidence related to the reaction mechanism on K/CeO$_2$ catalyst.*
692 *Applied Catalysis A-General 360* (1), 81-88. doi:10.1016/j.apcata.2009.03.011.

693 Gross, M.S., Ulla, M.A. & Querini, C.A. (2012). *Diesel particulate matter combustion with*
694 *CeO$_2$ as catalyst. Part I: System characterization and reaction mechanism. Journal of*
695 *Molecular Catalysis A: Chemical 352*, 86-94. doi:10.1016/j.molcata.2011.10.018.

696 Guillén-Hurtado, N., García-García, A. & Bueno-López, A. (2013). *Isotopic study of ceria-*
697 *catalyzed soot oxidation in the presence of NOx. Journal of Catalysis 299*, 181-187.
698 http://dx.doi.org/10.1016/j.jcat.2012.11.026.

699 Harrison, P.G., Ball, I.K., Daniell, W., Lukinskas, P., Céspedes, M., Miró, E.E. & Ulla, M.A.
700 (2003). *Cobalt catalysts for the oxidation of diesel soot particulate. Chemical Engineering*
701 *Journal 95* (1), 47-55. doi:10.1016/S1385-8947(03)00077-9.

702 Hirano, T., Tosho, T., Watanabe, T. & Akiyama, T. (2009). *Self-propagating high-*
703 *temperature synthesis with post-heat treatment of La$_{1-x}$Sr$_x$FeO$_3$ (x = 0-1) perovskite as*
704 *catalyst for soot combustion. Journal of Alloys and Compounds 470* (1-2), 245-249.
705 doi:10.1016/j.jallcom.2008.02.038.

706 Hong, S.S., Yang J.S. & Lee, G.D. (1999). *Catalytic combustion of carbon particulates over*
707 *perovskite-type oxides. Reaction Kinetics and Catalysis Letters 66* (2), 305-310.
708 10.1007/BF02475805

709 Hong S.S. & Lee G.D. (2006). *Catalytic removal of diesel soot particulates over LaMnO$_3$*
710 *perovskite-type oxides. Studies in Surface Science and Catalysis 159,* 261-264.
711 http://dx.doi.org/10.1016/S0167-2991(06)81583-1.

712 Jeguirim, M., Tschamber, V. & Ehrburger, P. (2007). *Catalytic effect of platinum on the*
713 *kinetics of carbon oxidation by NO$_2$ and O$_2$. Applied Catalysis B-Environmental 76* (3-4),
714 235-240. doi:10.1016/j.apcatb.2007.05.029.

715 Jelles, S.J., Neeft, J.P.A., Van Setten, B.A.A.L., Makkee, M. & Moulijn, J.A. (1998a).
716 *Improved soot oxidation by fuel additives and molten salt catalysts. Studies in Surface*
717 *Science and Catalysis 116*, 621-623. http://dx.doi.org/10.1016/S0167-2991(98)80917-8.

718 Jelles, S.J., Van Setten, B.A.A.L., Makkee, M. & Moulijn, J.A. (1998b). *Supported liquid*
719 *phase catalysts: A new approach for catalytic oxidation in diesel exhaust particulate*
720 *emission control. Studies in Surface Science and Catalysis 116,* 667-674.
721 http://dx.doi.org/10.1016/S0167-2991(98)80922-1.

722 Jelles, S.J., Van Setten, B.A.A.L., Makkee, M. & Moulijn, J.A. (1999). *Molten salts as*
723 *promising catalysts for oxidation of diesel soot: importance of experimental conditions in*
724 *testing procedures. Applied Catalysis B-Environmental 21,* 35-49.
725 http://dx.doi.org/10.1016/S0926-3373(99)00011-9.

726 Jelles, S.J., Krul, R.R., Makkee, M. & Moulijn, J.A. (1999b). *Improvement of Pt catalyst for*
727 *soot oxidation using mixed oxide as a support. Catalysis Today 53* (4), 623-630.
728 http://dx.doi.org/10.1016/S0920-5861(99)00150-9.

729 Kaspar, J., Fornasiero, P. & Graziani, M. (1999). *Use of CeO$_2$-based oxides in the three-way*
730 *catalysis. Catalysis Today* 50 (1999) 285-298. http://dx.doi.org/10.1016/S0920-
731 5861(98)00510-0.

732 Kayama, T., Yamazaki, K. & Shinjoh, H. (2010). *Nanostructured ceria-silver synthesized in a*
733 *one-pot redox reaction catalyzes carbon oxidation. Journal of the American Chemical*
734 *Society 132* (38), 13154-13155. DOI: 10.1021/ja105403x

735 Kimura, R., Elangovan, S. P., Ogura, M., Ushiyama, H. & Okubo T., (2011). *Alkali*
736 *Carbonate Stabilized on Aluminosilicate via Solid Ion Exchange as a Catalyst for Diesel*
737 *Soot Combustion. Journal of Physical Chemistry C 115*, 14892–14898.
738 dx.doi.org/10.1021/jp2034664.

739 Klein, J., Fechete, I., Bresset, V., Garin, F. & Tschamber, V. (2012). *Effect of carbon black*
740 *combustion on NOx trap catalyst performances. Catalysis Today 189* (1), 60-64.
741 doi:10.1016/j.cattod.2012.02.060

Klein, J., Wu, D., Tschamber, V., Fechete, I. & Garin, F. (2013). *Carbon-NSR catalyst interaction: Impact on catalyst structure and NOx storage efficiency. Applied Catalysis B-Environmental 132-133*, 527-534. http://dx.doi.org/10.1016/j.apcatb.2012.12.019.

Krishna, K. & Makkee, M. (2006). *Soot oxidation over NOx storage catalysts: Activity and deactivation. Catalysis Today 114*, 48–56. doi:10.1016/j.cattod.2006.02.009.

Krishna, K., Bueno-López, A., Makkee, M. & Moulijn, J.A. (2007). *Potential rare earth modified CeO_2 catalysts for soot oxidation. I. Characterisation and catalytic activity with O_2. Applied Catalysis B-Environmental 75* (3-4), 189-200. doi:10.1016/j.apcatb.2007.04.010.

Krishna, K., Bueno-López, A., Makkee, M. & Moulijn, J.A. (2007b). *Potential rare-earth modified CeO_2 catalysts for soot oxidation part II: Characterisation and catalytic activity with $NO + O_2$. Applied Catalysis B-Environmental 75* (3-4), 201-209. doi:10.1016/j.apcatb.2007.04.007.

Krishna, K., Bueno-López, A., Makkee, M. & Moulijn, J.A. (2007c). *Potential rare-earth modified CeO_2 catalysts for soot oxidation. Part III. Effect of dopant loading and calcination temperature on catalytic activity with O_2 and $NO + O_2$. Applied Catalysis B-Environmental 75* (3-4), 210-220. doi:10.1016/j.apcatb.2007.04.009.

Kureti, S., Weisweiler, W. & Hizbullah, K. (2003). *Simultaneous conversion of nitrogen oxides and soot into nitrogen and carbon dioxide over iron containing oxide catalysts in diesel exhaust gas. Applied Catalysis B-Environmental 43*, 281–291. http://dx.doi.org/10.1016/j.apcatb.2012.12.019

Kustov, A.L., Ricciardi, F. & Makkee, M. (2009). *NOx Storage and High Temperature Soot Oxidation on $Pt–Sr/ZrO_2$ Catalyst. Topics in Catalysis 52*, 2058–2062. DOI 10.1007/s11244-009-9394-y

Liang, Q., Wu, X., Weng, D. & Lu, Z (2007). *Selective oxidation of soot over Cu doped ceria/ceria-zirconia catalysts. Catalysis Communications 9* (2), 202-206. doi:10.1016/j.apcatb.2006.01.019.

Liang, Q., Wu, X., Weng, D. & Xu, H. (2008). *Oxygen activation on Cu/Mn-Ce mixed oxides and the role in diesel soot oxidation. Catalysis Today 139* (1-2), 113-118. doi:10.1016/j.cattod.2008.08.013.

Lin, H., Li, Y., Shangguan, W. & Huang, Z. (2009). *Soot oxidation and NOx reduction over $BaAl_2O_4$ catalyst. Combustion and Flame 156*, 2063–2070. doi:10.1016/j.combustflame.2009.08.006

Liu, S., Obuchi, A., Oi-Uchisawa, J., Nanba, T. & Kushiyama, S. (2001). *Synergistic catalysis of carbon black oxidation by Pt with MoO₃ or V₂O₅*. Applied Catalysis B-Environmental 30 (3-4), 259-265. http://dx.doi.org/10.1016/S0926-3373(00)00238-1.

Liu, J., Zhao, Z., Xu, C., Duan, A., Zhu, L. & Wang, X. (2006). *The structures of VOx/MOx and alkali-VOx/MOx catalysts and their catalytic performances for soot combustion. Catalysis Today 118*, 315–322. doi:10.1016/j.cattod.2006.07.015.

Liu, J., Zhao, Z., Xu, C. & Duan, A. (2008). *Simultaneous removal of NOx and diesel soot over nanometer Ln-Na-Cu-O perovskite-like complex oxide catalysts. Applied Catalysis B-Environmental 78*, 61–72. doi:10.1016/j.apcatb.2007.09.001

Liu, J., Zhao, Z., Chen, Y., Xu, C., Duan, A. & Jiang, G. (2011). *Different valent ions-doped cerium oxides and their catalytic performances for soot oxidation. Catalysis Today 175* (1), 117-123. doi:10.1016/j.cattod.2011.05.023

Liu, S., Wu, X., Weng, D. & Ran, R. (2012). *NOx-assisted soot oxidation on Pt-Mg/Al₂O₃ catalysts: Magnesium precursor, Pt particle size, and Pt-Mg interaction. Industrial and Engineering Chemistry Research 51* (5), 2271-2279. dx.doi.org/10.1021/ie202239c.

López-Suárez, F.E., Bueno-López, A., Illán-Gómez, M.J., Adamski, A., Ura, B. & Trawczynski, J. (2008). *Copper catalysts for soot oxidation: Alumina versus perovskite supports. Environmental Science and Technology 42* (20), 7670-7675. DOI: 10.1021/es8009293.

López-Suárez, F. E., Bueno-López A., Illán-Gómez, M. J., Ura, B. & Trawczynski J. (2009). *Potassium Stability in Soot Combustion Perovskite Catalysts. Topics in Catalysis 52*, 2097–2100. DOI 10.1007/s11244-009-9385-z.

Machida, M., Murata, Y., Kishikawa, K., Zhang, D. & Ikeue, K. (2008). *On the reasons for high activity of CeO₂ catalyst for soot oxidation. Chemistry of Materials 20* (13), 4489-4494. DOI: 10.1021/cm800832w.

Makkee, M., Krijnsen, H.C., Bertin, S.S., Calis, H.P.A., Van Den Bleek, C.M. & Moulijn, J.A. (2002). *Bench-scale demonstration of an integrated deSoot-deNOx system. Catalysis Today 75* (1-4), 459-464. http://dx.doi.org/10.1016/S0920-5861(02)00096-2.

Maricq, M. M. (2007). *Chemical characterization of particulate emissions from diesel engines: A review. Journal of Aerosol Science 38* (11), 1079-1118. http://dx.doi.org/10.1016/j.jaerosci.2007.08.001.

Matarrese, R., Castoldi, L., Lietti, L. & Forzatti, P. (2009). *Simultaneous removal of NOx and soot over Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃ DPNR catalysts. Topics in Catalysis 52* (13-20), 2041-2046. DOI 10.1007/s11244-009-9400-4.

McKee, D.W. *Mechanisms of the alkali metal catalysed gasification of carbon. Fuel.* (1983) 62, 170-175. http://dx.doi.org/10.1016/0016-2361(83)90192-8.

Mul, G., Neeft, J.P.A., Kapteijn, F., Makkee, M. & Moulijn, J.A. (1995). *Soot oxidation catalyzed by a Cu/K/Mo/Cl catalyst: Evaluation of the chemistry and performance of the catalyst. Applied Catalysis B-Environmental 6*, 339-352. http://dx.doi.org/10.1016/0926-3373(95)00027-5.

Mul, G., Kapteijn, F. & Moulijn, J.A. (1996). *Catalytic oxidation of model soot by metal chlorides. Applied Catalysis B-Environmental 12* (1), 33-47. http://dx.doi.org/10.1016/S0926-3373(96)00065-3.

Neeft, J.P.A., Makkee, M. & Moulijn J. A. (1996). *Diesel particulate emission control. Fuel Processing Technology 47* (1), 1-69. http://dx.doi.org/10.1016/0378-3820(96)01002-8.

Neeft, J.P.A., Makkee, M. & Moulijn J. A. (1996b). *Catalysts for the oxidation of soot from diesel exhaust gases. I. An exploratory study. Applied Catalysis B-Environmental 8*, 57-78. http://dx.doi.org/10.1016/0926-3373(95)00057-7.

Neri, G., Bonaccorsi, L., Donato, A., Milone, C., Musolino, M. G. & Visco, A.M. (1997). *Catalytic combustion of diesel soot over metal oxide catalysts. Applied Catalysis B-Environmental 11,* 217-231. http://dx.doi.org/10.1016/S0926-3373(96)00045-8

Neri, G., Rizzo, G., Galvagno, S., Donato, A., Musolino, M.G. & Pietropaolo, R. (2003). *K- and Cs-FeV/Al₂O₃ soot combustion catalysts for diesel exhaust treatment. Applied Catalysis B-Environmental 42*, 381–391. http://dx.doi.org/10.1016/S0926-3373(02)00271-0.

Moulijn, J.A., Cerfontain, M.B. & Kapteijn, F. (1984). *Mechanism of the potassium catalysed gasification of carbon in CO₂. Fuel*, 63, 1043-1047. http://dx.doi.org/10.1016/0016-2361(84)90185-6.

Oi-Uchisawa, J., Obuchi, A., Zhao, Z. & Kushiyama, S. (1998). *Carbon oxidation with platinum supported catalysts. Applied Catalysis B-Environmental 18*, L183-L187. http://dx.doi.org/10.1016/S0926-3373(98)00046-0.

Oi-Uchisawa, J., Obuchi, A., Enomoto, R., Liu, S., Nanba, T. & Kushiyama, S. (2000). *Catalytic performance of Pt supported on various metal oxides in the oxidation of carbon black. Applied Catalysis B-Environmental 26*, 17–24. http://dx.doi.org/10.1016/S0926-3373(99)00142-3.

Oi-Uchisawa, J., Wang, S., Nanba, T., Ohi, A. & Obuchi, A. (2003). *Improvement of Pt catalyst for soot oxidation using mixed oxide as a support. Applied Catalysis B-Environmental 44* (3), 207-215. doi:10.1016/S0926-3373(03)00055-9.

Peng, X., Lin, H., Shangguan, W. & Huang, Z. (2007). *A highly efficient and porous catalyst for simultaneous removal of NOx and diesel soot. Catalysis Communications 8* (2), 157-161. doi:10.1016/j.catcom.2006.04.015.

Peralta, M.A., Milt, V.G., Cornaglia, L.M. & Querini, C.A. (2006). *Stability of Ba,K/CeO$_2$ catalyst during diesel soot combustion: Effect of temperature, water, and sulfur dioxide. Journal of Catalysis 242* (1), 118-130. doi:10.1016/j.jcat.2006.05.025.

Pieta, I.S., García-Diéguez, M., Herrera, C., Larrubia, M.A. & Alemany, L.J. (2010). *In situ DRIFT-TRM study of simultaneous NOx and soot removal over Pt-Ba and Pt-K NSR catalysts. Journal of Catalysis 270* (2), 256-267. doi:10.1016/j.jcat.2010.01.003.

Reddy, B.M., Bharali, P., Thrimurthulu, G., Saikia, P., Katta, L. & Park, S.-E. (2008). *Catalytic efficiency of ceria-zirconia and ceria-hafnia nanocomposite oxides for soot oxidation. Catalysis Letters 123* (3-4), 327-333. DOI 10.1007/s10562-008-9427-3.

Russo, N., Fino, D., Saracco, G. & Specchia, V. (2005). *Studies on the redox properties of chromite perovskite catalysts for soot combustion. Journal of Catalysis* 229, 459–469. doi:10.1016/j.jcat.2004.11.025.

Russo, N., Fino, D., Saracco, G. & Specchia, V. (2008). *Promotion effect of Au on perovskite catalysts for the regeneration of diesel particulate filters. Catalysis Today 137* (2-4), 306-311. doi:10.1016/j.cattod.2007.09.010.

Russo, N., Furfori, S., Fino, D., Saracco, G. & Specchia, V. (2008b). *Lanthanum cobaltite catalysts for diesel soot combustion. Applied Catalysis B-Environmental 83*, 85–95. doi:10.1016/j.apcatb.2008.02.006.

Sánchez Escribano, V., Fernández López, E., Gallardo-Amores, J.M., del Hoyo Martínez, C., Pistarino, C., Panizza, M., Resini, C. & Busca, G. (2008). *A study of a ceria-zirconia-supported manganese oxide catalyst for combustion of Diesel soot particles. Combustion and Flame 153* (1-2), 97-104 . doi:10.1016/j.combustflame.2007.11.010

Setiabudi, A., Van Setten, B.A.A.L., Makkee, M. & Moulijn, J.A., (2002). *The influence of NOx on soot oxidation rate: molten salt versus platinum. Applied Catalysis B-Environmental 35,* 159–166. http://dx.doi.org/10.1016/S0926-3373(01)00251-X.

Setiabudi, A., Chen, J., Mul, G., Makkee, M. & Moulijn, J.A. (2004). *CeO$_2$ catalysed soot oxidation: The role of active oxygen to accelerate the oxidation conversion. Applied Catalysis B-Environmental 51* (1), 9-19. doi:10.1016/j.apcatb.2004.01.005.

Shangguan, W.F., Teraoka, Y. & Kagawa, S. (1996). *Simultaneous catalytic removal of NOx and diesel soot particulates over ternary AB$_2$O$_4$ spinel-type oxides. Applied Catalysis B-Environmental 8* (2), 217-227. http://dx.doi.org/10.1016/0926-3373(95)00070-4.

Shangguan, W.F., Teraoka, Y. & Kagawa, S. (1998). *Promotion effect of potassium on the catalytic property of CuFe$_2$O$_4$ for the simultaneous removal of NOx and diesel soot particulate. Applied Catalysis B-Environmental 16*, 149-154. http://dx.doi.org/10.1016/S0926-3373(97)00068-4.

Teraoka, Y., Nakano, K., Kagawa, S. & Shangguan, W.F. (1995). *Simultaneous removal of nitrogen oxides and diesel soot particulates catalyzed by perovskite-type oxides. Applied Catalysis B-Environmental 5* (3), L181-L185. http://dx.doi.org/10.1016/0926-3373(94)00059-X.

Teraoka, Y., Nakano, K., Shangguan, W. & Kagawa, S. (1996). *Simultaneous catalytic removal of nitrogen oxides and diesel soot particulate over perovskite-related oxides. Catalysis Today 27* (1-2), 107-113. http://dx.doi.org/10.1016/0920-5861(95)00177-8.

Teraoka, Y.,Kanada, K. & Kagawa, S. (2001). *Synthesis of La–K–Mn–O perovskite-type oxides and their catalytic property for simultaneous removal of NOx and diesel soot particulates. Applied Catalysis B-Environmental 34*, 73–78. http://dx.doi.org/10.1016/S0926-3373(01)00202-8.

Tikhomirov, K., Kröcher, O., Elsener, M. & Wokaun, A. (2006). *MnOx-CeO$_2$ mixed oxides for the low-temperature oxidation of diesel soot. Applied Catalysis B-Environmental 64* (1-2) 72-78. doi:10.1016/j.apcatb.2005.11.003.

Twigg, M.V. (2006). *Roles of catalytic oxidation in control of vehicle exhaust emissions. Catalysis Today 117* (4), 407-418. doi:10.1016/j.cattod.2006.06.044.

Twigg, M.V. (2007). *Progress and future challenges in controlling automotive exhaust gas emissions. Applied Catalysis B-Environmental 70*, 2–15. doi:10.1016/j.apcatb.2006.02.029.

Ura, B., Trawczynski, J., Kotarba, A., Bieniasz, W., Illán-Gómez M.J., Bueno-López, A. & López-Suárez, F.E. (2011). *Effect of potassium addition on catalytic activity of SrTiO$_3$ catalyst for diesel soot combustion. Applied Catalysis B-Environmental 101*, 169–175. doi:10.1016/j.apcatb.2010.09.018.

Van Craenenbroeck, J., Andreeva, D., Tabakova, T., Van Werde, K., Mullens, J. & Verpoort, F. (2002). *Spectroscopic analysis of Au-V-based catalysts and their activity in the catalytic removal of diesel soot particulates. Journal of Catalysis 209* (2), 515-527. doi:10.1006/jcat.2002.3649.

Van Setten, B.A.A.L., Bremmer, J., Jelles, S.J., Makkee, M. & Moulijn, J.A. (1999). *Ceramic foam as a potential molten salt oxidation catalyst support in the removal of soot from diesel exhaust gas. Catalysis Today 53* (4), 613-621. http://dx.doi.org/10.1016/S0920-5861(99)00149-2.

Van Setten, B.A.A.L., Van Dijk, R., Jelles, S.J., Makkee, M. & Moulijn, J.A. (1999b). *The potential of supported molten salts in the removal of soot from diesel exhaust gas. Applied Catalysis B-Environmental 21*, 51-61. http://dx.doi.org/10.1016/S0926-3373(99)00008-9.

Van Setten, B.A.A.L., Schouten, J.M., Makkee, M. & Moulijn, J.A. (2000). *Realistic contact for soot with an oxidation catalyst for laboratory studies. Applied Catalysis B-Environmental 28* (3-4), 253-257. http://dx.doi.org/10.1016/S0926-3373(00)00182-X.

Van Setten, B.A.A.L., Makkee, M. & Moulijn, J.A. (2001). *Science and technology of catalytic diesel particulate filters. Catalysis Reviews - Science and Engineering 43* (4), 489-564. DOI: 10.1081/CR-120001810

Van Setten, B.A.A.L., Van Gulijk, C., Makkee, M. & Moulijn, J.A. (2001b). *Molten salts are promising catalysts. How to apply in practice?. Topics in Catalysis 16-17* (1-4), 275-278. DOI: 10.1023/A:101664461203.

Van Setten, B.A.A.L., Spitters, C.G.M., Bremmer, J., Mulders, A.M.M., Makkee, M. & Moulijn, J.A. (2003). *Stability of catalytic foam diesel-soot filters based on Cs_2O, MoO_3, and Cs_2SO_4 molten-salt catalysts. Applied Catalysis B-Environmental 42* (4), 337-347. http://dx.doi.org/10.1016/S0926-3373(02)00265-5.

Villani, K., Kirschhock, C.E.A., Liang, D., Van Tendeloo, G. & Martens, J.A. (2006). *Catalytic carbon oxidation over ruthenium-based catalysts. Angewandte Chemie - International Edition 45* (19), 3106-3109. DOI: 10.1002/anie.200503799.

Wang, H., Zhao, Z., Liang, P., Xu, C., Duan, A., Jiang, G., Xu, J. & Liu, J., (2008). *Highly Active $La_{1-x}K_xCoO_3$ Perovskite-type Complex Oxide Catalysts for the Simultaneous Removal of Diesel Soot and Nitrogen Oxides Under Loose Contact Conditions. Catalysis Letters. 124*, 91–99. DOI 10.1007/s10562-008-9429-1.

Wei, Y., Liu, J., Zhao, Z., Xu, C., Duan, A. & Jiang, G. (2013). *Structural and synergistic effects of three-dimensionally ordered macroporous $Ce_{0.8}Zr_{0.2}O_2$-supported Pt nanoparticles*

937 *on the catalytic performance for soot combustion. Applied Catalysis A-General 453*, 250-
938 261. http://dx.doi.org/10.1016/j.apcata.2012.12.013

939 Wu, X., Liang, Q., Weng, D. & Lu, Z. (2007). *The catalytic activity of CuO–CeO$_2$ mixed*
940 *oxides for diesel soot oxidation with a NO/O$_2$ mixture. Catalysis Communications 8,* 2110–
941 2114. doi:10.1016/j.catcom.2007.04.023.

942 Xu, J., Liu, J., Zhao, Z., Zheng, J., Zhang, G., Duan, A. & Jiang, G. (2010b). *Three-*
943 *dimensionally ordered macroporous LaCo$_x$Fe$_{1-x}$O$_3$ perovskite-type complex oxide catalysts*
944 *for diesel soot combustion. Catalysis Today 153* (3-4), 136-142.
945 doi:10.1016/j.cattod.2010.01.063.

946 Yao, W., Wang, R. & Yang, X. (2009). *LaCo$_{1-x}$Pd$_x$O$_3$ perovskite-type oxides: Synthesis,*
947 *characterization and simultaneous removal of NOx and Diesel Soot. Catalysis Letters 130*
948 (3-4), 613-621. DOI 10.1007/s10562-009-9905-2.

949 Zawadzki, M., Staszak, W., López-Suárez, F.E., Illán-Gómez, M.J. & Bueno-López, A.
950 (2009). *Preparation, characterisation and catalytic performance for soot oxidation of*
951 *copper-containing ZnAl$_2$O$_4$ spinels. Applied Catalysis A-General 371* (1-2), 92-98.
952 doi:10.1016/j.apcata.2009.09.035.

953 Zawadzki, M., Walerczyk, W., López-Suárez, F.E., Illán-Gómez, M.J. & Bueno-López, A.
954 (2011). *CoAl$_2$O$_4$ spinel catalyst for soot combustion with NOx/O$_2$. Catalysis*
955 *Communications 12* (13), 1238-1241. doi:10.1016/j.catcom.2011.04.021.

956 Zhang-Steenwinkel, Y., Van Der Zande, L.M., Castricum, H.L., Bliek, A., Van Den Brink,
957 R.W. & Elzinga, G.D. (2005). *Microwave-assisted in-situ regeneration of a perovskite*
958 *coated diesel soot filter. Chemical Engineering Science 60* (3), 797-804.
959 doi:10.1016/j.ces.2004.09.042.

960 Zhang, G., Zhao, Z., Liu, J., Jiang, G., Duan, A., Zheng, J., Chen, S. & Zhou, R. (2010).
961 *Three dimensionally ordered macroporous Ce$_{1-x}$Zr$_x$O$_2$ solid solutions for diesel soot*
962 *combustion. Chemical Communications 46*, 457–459. DOI: 10.1039/B915027G.

963 Zhang, G., Zhao, Z., Liu, J., Xu, J., Jing, Y., Duan, A. & Jiang, G. (2010b). *Macroporous*
964 *perovskite-type complex oxide catalysts of La$_{1-x}$K$_x$Co$_{1-y}$Fe$_y$O$_3$ for diesel soot combustion.*
965 *Journal of Rare Earths 27* (6), 955-960. http://dx.doi.org/10.1016/S1002-0721(08)60369-5.

966 Zheng, J., Liu, J., Zhao, Z., Xu, J., Duan, A. & Jiang, G. (2012). *The synthesis and catalytic*
967 *performances of three-dimensionally ordered macroporous perovskite-type LaMn$_{1-x}$Fe$_x$O$_3$*
968 *complex oxide catalysts with different pore diameters for diesel soot combustion. Catalysis*
969 *Today 191* (1), 146-153. doi:10.1016/j.cattod.2011.12.013.

970 Zhu, L., Yu, J. & Wang, X. (2007). *Oxidation treatment of diesel soot particulate on Ce$_x$Zr$_{1-}$*

971 *$_x$O$_2$.* *Journal* *of* *Hazardous* *Materials* *140* (1-2), 205-210.

972 doi:10.1016/j.jhazmat.2006.06.055.