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Soot combustion over silver-supported catalysts

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ABSTRACT

In this study the characterization and soot oxidation activity of Ag-based catalysts deposited on alumina, ceria and zirconia have been investigated. The combustion of soot was shown to be promoted by the presence of silver, especially in a zero valent state, over all the supports investigated. Presence of silver in a positive oxidation state is favoured with CeO_2, while zero valent silver dominates over alumina and zirconia. This is likely attributed to the oxygen storage capacity of ceria which stabilizes silver in an oxidized form. Soot oxidation starts at low temperature (around 500 K for Ag on ZrO_2) with a T_{50} in the range of 600–640 K. Deactivation under strong ageing conditions (1023 K for 12 h) is negligible with alumina and zirconia, while in the presence of ceria, which slows down formation of metallic silver from Ag_2O, loss of activity following thermal treatments at high temperatures becomes more intense.

1. Introduction

It is widely recognized that diesel engine vehicles are fated to significantly increase their worldwide penetration, even in countries where the present market share is not remarkable as that of gasoline engines. Exhaust abatement in diesel engines poses a series of challenges to meet new legislation especially for NO_x and particulate reduction [1–3]. The severity of regulation requires solutions based on de-NO_x systems and catalytic traps for either light and heavy duty engines.

The most effective and widely applied after-treatment technology for the particulate matter (PM) control is based on diesel particulate filter (DPF) [4–6]. These devices perform the filtration of exhaust gases by removing a significant fraction of particulate, which adheres to the filter walls; they must be periodically regenerated to remove the entrapped soot and avoid increase of pressure drop at the exhaust.

The regeneration process can be carried out by combustion of PM by injection of extra fuel; this, however, implies an extra fuel consumption, which reduces the engine efficiency; moreover, excessive heating can damage both filter and the other after-treatment devices (i.e. the de-NO_x catalysts). Therefore remarkable research efforts have been made to find alternative solution for filter regeneration at lower temperature.

In one approach, a catalyst is deposited on the filter media which allows regeneration to occur in a continuous or periodic manner, during the regular operation of the system [1]. The main purpose of the catalyst is therefore to facilitate a passive regeneration of the filter by enabling the oxidation of diesel PM under exhaust temperatures reached during regular operation of the engine/vehicle, typically in the 573–673 K range. In the absence of the catalyst, particulates can be oxidized at appreciable rates only at temperatures around 800–900 K, which can occur only at full load conditions. Catalytic approach is affected by several drawbacks: catalytic filter regeneration is very complex because of the very variable conditions of reaction; moreover, the process is quite slow because of the poor soot/catalyst contact. Another important operative constraint is represented by the wide range of temperature expected for the exhausted gases (from 473 to 873 K), depending upon engine load. Consequently a useful catalyst has to operate efficiently at low temperatures but has also to be thermally stable.

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Diverse catalytic materials have been studied in the last years based on different properties. One approach is to increase the contact points between the soot particle and the catalysts by using fuel borne catalyst additives or molten salt catalysts which can wet the soot surface and therefore decrease the oxidation temperature [7–9]. The use of a more powerful oxidant than oxygen, like NO_2, can also efficiently decrease the soot combustion temperature [10–12]. Among the several catalyst components used for soot oxidation the most promising formulations are based on addition of potassium to oxides of transition metals (such as Cu, V, Mo, Co or Fe) [8,9,13–17], or on systems based on combination of Co, K/MgO or Ba, K/CeO_2 [11,18,19], or on the use of perovskites like $La_{1-x}Cs_xCoO_3$, $LaMnO_3$, and $La_{0.9}K_{0.1}Cr_{0.9}O_{3-\gamma}$ [20]. Several supports like ZrO_2, TiO_2, Al_2O_3 and CeO_2 have also been reported for use in diesel soot oxidation. Ceria alone or in combination with other oxides is active in oxidation of carbon particles [11,12,21–33] and the mechanism of action is associated to the redox activity of the material; that is the effectiveness of the catalyst can be related to its ability to deliver oxygen from the lattice to the gas phase (or better to the soot reactant) in a wide temperature range. It has been reported that the use of supports based on cerium oxide confers interesting properties to soot combustion catalysts due to high availability of surface oxygen and high surface reducibility [24,25,32,33]. The success of oxygen storage systems based on ceria is due to their ability to change oxidation state during operation (i.e. CeO_2 to CeO_{2-x}) maintaining structural integrity, thus allowing oxygen uptake and release to occur easily. The use of CeO_2-supported metals can increase the benefit of bare ceria due to the establishment of an interaction between the metal and the support that enhances the redox characteristics of pure ceria [10,11,25,34,35]. In addition, a mechanism in which the redox of CeO_2 contributes to the generation of superoxide species in a more efficient manner compared to other oxides has been recently put forward to explain higher reactivity among a series of catalyst supports [36].

Silver is known to be an efficient partial oxidation catalyst and it is industrially used for epoxidation of ethylene to ethylene epoxide [37,38] and for oxi-dehydrogenation of methanol to formaldehyde [39–41]. Other applications in which Ag has shown remarkable performances include NO_x abatement [42,43], ammonia oxidation [44] and oxidation of methane, carbon monoxide and organic volatile compounds [45–47]. The use of Ag deposited on ceria was also found to increase the rate of carbon gasification compared to other noble metals [48] establishing a sort of enhanced metal–support interaction. Recently the potential of silver on alumina catalyst for the oxidation of carbon particle in the presence of NO_x and oxygen has been also reported [49].

These properties stimulated us to investigate in detail the behaviour of silver deposited on ceria in the oxidation of carbon soot particles. The study was also extended to other supports like alumina and zirconia, that were also reported to be effective in several oxidation reaction in the presence of Ag [38,40,42,44,49]. The aim is to obtain a better understanding of Ag/Ag-oxide chemistry and their interaction with the support as related to soot oxidation reaction. We have found that these catalytic materials are able to perform carbon oxidation at temperature as low as 600 K, as studied by temperature programmed oxidation and thermogravimetric methods. Structural details, monitored by HRTEM and XRD, allowed us to distinguish also the effect of different supports on the behaviour of supported Ag/Ag_2O particles.

2. Experimental procedures

2.1. Materials

Silver-doped catalysts (1–10 wt%) were prepared by incipient wetness impregnation of CeO_2, ZrO_2 and γ-Al_2O_3 (Grace Davison),

Table 1
Characteristics of samples used in this study.

Sample	Ag (wt%)	Surface area (m^2/g)	
		Fresh	Aged[a]
CeO_2	–	49	22
Ce1Ag	1	47	12
Ce5Ag	5	37	13
Ce10Ag	10	34	13
ZrO_2	–	59	27
Zr1Ag	1	48	20
Zr5Ag	5	45	19
Zr10Ag	10	39	16
Al_2O_3	–	180	159
Al1Ag	1	175	158
Al5Ag	5	165	157
Al10Ag	10	156	153

[a] After treatment under air at 1023 K for 12 h.

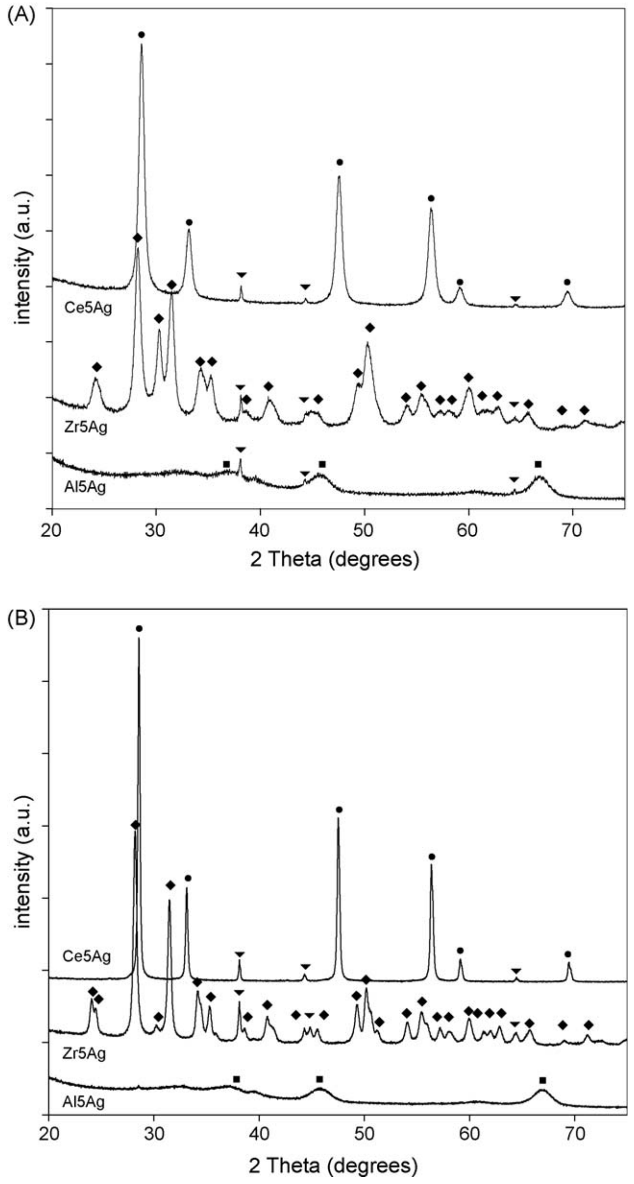

Fig. 1. XRD profiles of fresh (A) and aged (B) samples: Ag, ▼; CeO_2, ●; ZrO_2, ◆; Al_2O_3, ■.