Ag-based catalysts for diesel soot combustion

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Introduction

In the last years, the attention on negative effects of Diesel particulate matter on health has rapidly grown and the laws on emission become more stringent. Among the several techniques that have been developed for reducing particulate emissions from diesel engines, filtering followed by catalytic oxidation is one of the more promising. In the catalytic approach the system is based on the use of a catalyst to achieve the onset of regeneration at a significantly lower temperature. Recently, 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 [1-4]. The introduction of dopants/promoters has been shown to increase the catalytic efficiency of ceria, in terms of anticipated onset of combustion and thermal resistance [5-6]. The main objective of our study was to investigate the effect of adding silver as promoter on oxides comprising cerium oxide, zirconium oxide and alumina.

Materials and Methods

Silver doped catalysts were prepared by incipient wetness impregnation of CeO_2, ZrO_2 and Al_2O_3 with an aqueous solution of $AgNO_3$. They were dried at 373 K overnight and calcined in air at 773 K for 3 h (fresh samples) and at 1023 K for 12h (aged samples). All samples were characterized by conventional techniques (XRD, TPR, TGA, BET, HRTEM); soot oxidation was carried out by running temperature programmed oxidation experiments (TPO) and Thermal analysis (TGA) under controlled conditions over soot (Printex-U, Degussa AG)-catalyst mixtures.

Results and Discussion

The main results indicate that a remarkable decrease of oxidation temperature is observed by adding silver, regardless of the support used. The best results in terms of anticipated onset of combustion is observed with Ag/ZrO_2 where soot oxidation starts at around 230 °C for fresh samples and 250 °C for aged systems.
HRTEM and XRD results indicate that the active site is metallic silver; the mechanism of soot oxidation over Ag-doped catalysts likely includes dissociative adsorption of oxygen by formation of silver sub-oxide species, that are more active than molecular oxygen in soot combustion.
The resistance of catalysts to ageing shows that while ceria-based materials loose their activity upon calcination, samples based on zirconia and alumina are not affected by thermal treatments. Figure 1 shows the temperature at which 50% of weight loss is observed in TGA experiments (T_{50}, corresponding to the temperature at which 50% of soot is converted under tight contact conditions).
This behavior could be explained by a different interaction between silver and the support: the transformation $Ag_2O \rightarrow Ag$ during calcination of the sample is retarded in the presence of CeO_2 (Figure 2 shows that Ag_2O is still present after calcination in air at 750 °C for 12h); in zirconia and alumina systems there is more Ag in metallic state than Ag_2O in comparison with the ceria-based system and consequently more active sites available for the reaction.

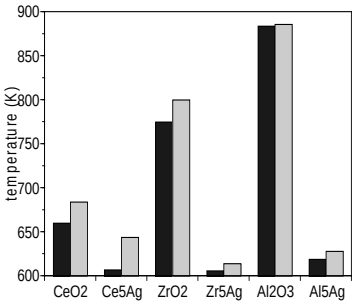

Figure 1. TGA results for both fresh and aged samples

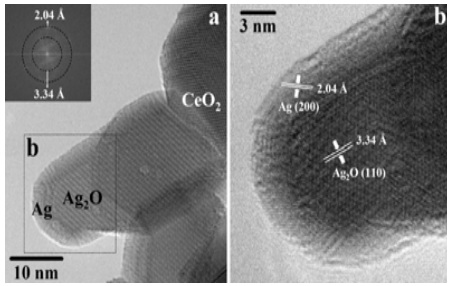

Figure 2. HRTEM feature of Ag/CeO_2 aged sample

Significance

Activity of Ag-doped systems in terms of T_{50} are among the highest observed in the literature and therefore they represent an extremely promising class of catalysts.

References

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