$Ag/Ce_{1-x}Mn_xO_2$ Catalysts for Soot Oxidation: Role of Ce/Mn Molar Ratio

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Significance and Relevance

This study highlights the development of Ag/CeO_2, Ag/MnO_x, and $Ag/CeMnO_x$ catalysts prepared via the citrate sol-gel method, focusing on their efficacy in soot oxidation. The novel nanodomain structure in $CeMnO_x$, influenced by the Ce/Mn ratio, enhances catalytic activity and stability, particularly at a 1:1 ratio, which prevents CeO_2 sintering. The catalysts demonstrate selective soot oxidation to CO_2 at relatively low temperatures (<500°C for powders and <600°C for monoliths), showcasing their practical potential. Additionally, the findings reveal NO inhibitory effects on oxidation, mitigated by CO in $NO+O_2$ mixtures, offering valuable insights for emission control technologies.

Preferred and 2nd choice for the topic: Automotive and stationary emission control; Air cleaning and combustion.
Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Diesel engines, known for their strong power performance and high fuel efficiency, are considered a promising power source for light vehicles, which have predominantly relied on gasoline engines. However, a widespread adoption of diesel engines is hindered by significant emission issues, particularly the release of particulate matter (PM) mainly composed of soot. The use of catalytic filters, specifically diesel particulate filters (DPFs), which trap and oxidize soot effectively reducing its harmful impact by significantly lowering the soot oxidation temperature. CeO_2 is highly regarded for its exceptional catalytic activity and redox behavior. [1] Similarly, MnO_x is widely utilized in oxidation and reduction reactions, thanks to its multivalent oxidation states (mainly Mn^{2+}, Mn^{3+}, and Mn^{4+}) and the high mobility of lattice oxygen.[2] When combined, MnO_x-CeO_2 catalysts demonstrate superior catalytic activity significantly lowering the ignition temperature for soot oxidation due to the synergistic effect between the two metal oxides. [3] Furthermore, the addition of silver to the CeO_2 and MnO_x catalyst significantly boosts its reactivity for soot oxidation. [4] The aim of this study was to evaluate the performance of the $Ag/CeMnO_x$ catalysts in soot combustion under tight and loose contact conditions flowing 10 vol.% O_2/He as well as in the presence of NO and NO-CO.

Materials and Methods

Oxide supports were prepared by the citrate sol-gel method, using $Ce(NO_3)_3 \cdot 6H_2O$ and $Mn(NO_3)_2 \cdot 6H_2O$ as precursors in Ce/Mn molar ratios equal to 1/3, 1/1 or 3/1, after drying were calcined at 500°C. Ag catalysts (1 wt.%) were prepared by wet impregnation using $Ag(NH_3)_2$ and were calcined at 500 °C. The resulting samples were labeled as Ag/Ce, Ag/Mn and Ag/1Ce3Mn, Ag/1Ce1Mn and Ag/3Ce1Mn. Portions of the catalysts were treated in oven at 650°C for 12 h in order to simulate thermal aging.
Characterization by XRD, N_2 physisorption, XRF, Raman, SEM and TEM techniques was performed. Catalytic tests were carried out under tight and loose contact conditions in temperature-programmed

reaction (TPR) mode, under a flow of 10 vol.% O_2/He, 10 vol.% O_2, 0.1 vol.% NO/He, or 10 vol.% O_2, 0.1 vol.% NO, 1.25 vol.% CO/He.

Results and Discussion

Fig. 1a shows that in the presence of the supported Ag catalysts the temperature of soot oxidation significantly decreased with respect to the not catalyzed process. Moreover, in the presence of catalysts soot was fully oxidized to CO_2, while without any catalyst CO and CO_2 are formed. The Ag/Mn and Ag/1Ce3Mn samples demonstrated the lowest activity (~50% of soot conversion was achieved at around 500°C). A further increase in the Ce content in the oxide matrix resulted in the improvement of the catalyst activity, the Ag/Ce sample showing the highest activity (Tmax=448°C). Thermal aging at 650°C for 12 h lead to a significant deactivation of the Ag/Ce (aged) (Tmax=529°C) due to a strong decrease of the specific surface area and an increase in the crystallites size. The Tmax of soot oxidation over Ag/3Ce1Mn (aged) increased to 500°C (ΔTmax=37° C), while the Ag/1Ce1Mn (aged) appeared the most stable with the best oxidation performance (Tmax=465°C, ΔTmax=7° C), (Fig. 1b).

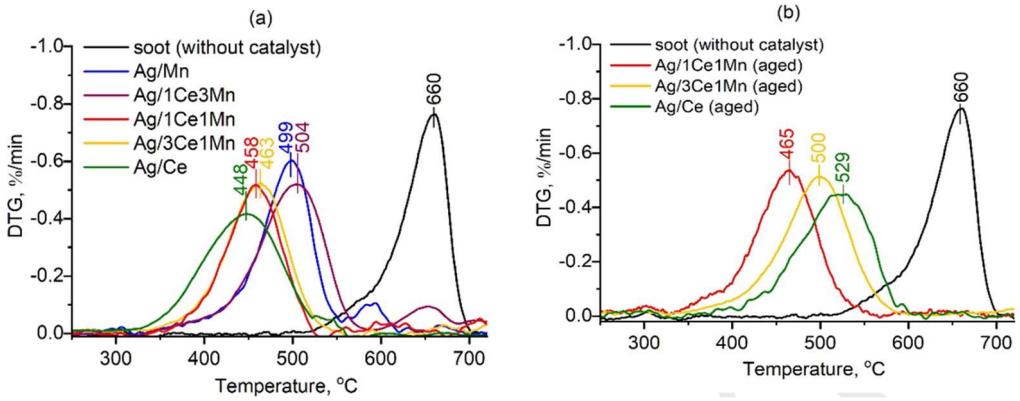

Figure 1. Soot oxidation activity versus temperature for fresh Ag supported catalysts (a) and those aged at 650 °C for 12 h (b).

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