Synergy of Ag and Yttria-Stabilized Zirconia catalysts during diesel soot oxidation

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Introduction

Motivated by increasingly stringent emissions regulations, Diesel Particulate Filters (DPFs) have seen widespread used as the only technically and economically feasible means for meeting current and future Particulate Matter (PM) emissions limits. DPFs present high filtering efficiency (>99%) but must be periodically regenerated due to soot particles accumulation [1]. EURO 6 standards require the utilization of a NOx catalytic after-treatment device [2], preferentially placed between the Diesel Oxidation Catalyst (DOC) and the DPF [2]. Therefore, NO_2 cannot anymore be utilized as an oxidant for soot combustion. This makes crucial the development of effective catalysts for soot combustion with oxygen, combining (i) activity at low temperatures and (ii) an excellent stability at high temperatures for complying the necessary durability.

We have recently reported that Yttria-stabilized Zirconia (YSZ), a pure oxygen ion ceramic conductor without any redox property, is a promising catalyst to continuously oxidize soot with oxygen in Diesel exhaust conditions [3]. Isotopic Temperature-Programmed Oxidation (TPO) [3] and isothermal catalytic oxidation experiments [4] using labeled oxygen $^{18}O_2$ demonstrated the key-role of bulk oxygen species in the soot oxidation process, when YSZ/soot were in 'tight' contact mode. It was proposed that the ignition of the soot oxidation on YSZ involves a fuel-cell-type electrochemical mechanism at the nanometric scale. The efficiency of this process strongly depends both on the YSZ/soot contact and also on the oxygen partial pressure. The 'tight' catalyst/ soot contact is not representative of the contact obtained inside DPFs. The target of this study is to further improve the YSZ soot oxidation efficiency when the catalyst/soot mixture is in the 'loose' contact. Silver efficiency for soot oxidation is based on its ability to deliver oxygen from the lattice/surface to the soot particle in a wide temperature range [5], combining that with its high mobility, during the oxidation process, makes it a good candidate for our goal. Therefore, Ag nanoparticles were deposited on YSZ from a Ag colloidal suspension. The catalytic performances for soot oxidation of these catalysts were compared with those of bare YSZ and Ag/γ-Al_2O_3 as a reference material both in "tight" and "loose" contact mode. In addition, different characterizations (TEM, TPR, XPS and isotopic exchange) were also conducted to elucidate the Ag/YSZ interactions.

Materials and Methods

Silver nanoparticles deposited on YSZ and γ-Al_2O_3 were synthesized using a modified polyol reduction method [6]. A colloid of Ag nanoparticles was first synthesized in ethylene glycol (anhydrous 99.8% Sigma Aldrich), starting from $AgNO_3$ (Alfa Aesar, 99.9% metals basis) precursor salt, in the presence of PVP (Sigma, 10,000 average molecular weight) and adding 0.0002 M NaOH (EM Science, ACS grade). The molar ratio of PVP to Ag was 1:1 by mass. The solution was stirred for 30 min at room temperature and subsequently refluxed for 2 h at 160°C. The resulting colloidal solution was deposited on YSZ (Tosoh, 13 $m^2 \cdot g^{-1}$) and γ-Al_2O_3 (Alfa-Aesar, 120 $m^2 \cdot g^{-1}$) supports for a desired metal loading of 1 wt%. The supported nanoparticles were extensively washed with deionized water and separated by centrifugation, then dried in air using a freeze dryer for 3-4 h.

TPO experiments were performed with 5% O_2 (LINDE gas, 99.995% purity) in helium with a heating ramp of 10°C/min from room temperature to 750°C in a fixed-bed tubular quartz reactor (internal diameter = 8 mm) with an overall flow of 8 L/h. The catalyst (20mg) and soot (model PRINTEX-U, 5mg) were in 'loose' contact mode (i.e. the catalyst–soot mixture was prepared by gently shaking it with a spatula in a polyethylene vessel for around 1-2 min) and in "tight" contact mode. CO_2 production rates were monitored by using a CO_2 infrared analyzer (HORIBA 3000), while CO production rates were measured using a micro-gas chromatograph (SRA 3000).

Results and Discussion

Catalytic performances of Al_2O_3, YSZ, 1wt% Ag/YSZ and Ag/Al_2O_3 for soot combustion in "loose" contact mode are presented in **Figure 1.** Silver supported catalysts only produced CO_2. When YSZ is used as a catalyst support, performances aremuch greater as the oxidation peak~~s~~ is observed at 500°C which is 75°C lower than on Ag/Al_2O_3. These results propose that a synergy between the oxidation processes of Ag and YSZ is taking place.

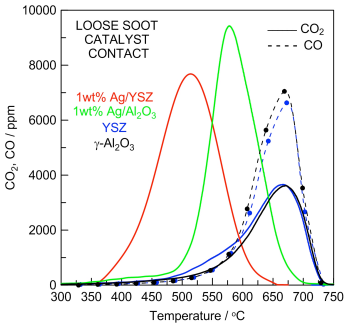

Figure 1. CO_2 and CO production rates as a function of temperature during the soot combustion on YSZ, Al_2O_3, 1wt % Ag/YSZ and Ag/Al_2O_3.

Significance

The addition of Ag nanoparticles on YSZ or γ-Al_2O_3 strongly improves the catalytic performances for soot oxidation in realistic conditions ("poor or loose" contact mode). This enhancement is much more pronounced on YSZ due specific interactions between Ag nanoparticles and the oxygen ionic conductor in linked with the fuel-cell-type electrochemical mechanism.

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