Investigations of soot combustion on Yttria-Stabilized Zirconia by Environmental Transmission Electron Microscopy (ETEM)

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Introduction

Diesel Particulate Filters (DPFs) equip all Diesel light vehicles in Europe to remove toxic Particulate Matter (PM). They present high filtering efficiency (>99%) but must be periodically regenerated due to soot particles accumulation. In addition, from 2014, EURO 6 standards require the utilization of a NOx catalytic after-treatment device [1], preferentially placed between the Diesel Oxidation Catalyst (DOC) and the DPF [1]. Therefore, NO_2 cannot anymore be utilized as an oxidant for soot combustion. This makes crucial the development of effective and durable catalysts for soot combustion with oxygen. We have recently reported that Yttria-stabilized Zirconia (YSZ), a pure oxygen ion ceramic conductor without any redox property, can continuously oxidize soot with oxygen in Diesel exhaust conditions [2]. It was proposed that the ignition of the soot oxidation on YSZ involves a fuel-cell-type electrochemical mechanism at the nanometric scale. Electrochemical oxidation of the soot could occur at the soot/YSZ interface while oxygen electrochemical reaction takes place at the triple phase boundary (tpb) soot/gas/YSZ. To get further insights of this mechanism, Environmental Transmission Electron Microscopy (ETEM) was used to in-situ follow the soot combustion at the interface with YSZ.

Materials and Methods

In situ, environmental experiments were performed in the Ly-EtTEM microscope, a last generation ETEM (TITAN 80-300 kV from FEI™) equipped with an aberration corrector. Pure oxygen was introduced owing to the high precision leaking valves at low pressure, up to typically 3 mbar. Samples prepared as a mixture of soot and YSZ particles (as described below) were deposited on titania grids with and without supporting film. These grids were subsequently mounted on a Gatan™ heating stage in inconel; the temperature was raised up to typically 550°C. The microscope was operated at 80 and 300 kV. Soot was obtained from a mini Combustion Aerosol Standard (miniCAST, Jing Ltd. Switzerland) soot generator. The soot particles were produced with a mini-CAST burner from a propane/air flame. This mini-CAST soot shows an EC (Elemental Carbon) /TC (Total Carbon) ratio of ~0.95, closed to that reported in the literature for real Diesel soots [3]. Yttria-stabilized Zirconia (YSZ) powder, containing 8 mole % of Yttria from TOSOH, $(ZrO_2)_{0.92}(Y_2O_3)_{0.08}$, was used as purchased. Collected soot and YSZ powder were mixed with a weight ratio of 1:4 and crushed for 20 minutes in a mortar in order to improve the soot/YSZ agglomerate contact, conventionally denoted as tight contact mode.

Results and Discussion

The soot/YSZ mixture was heated up to 550°C under vacuum. Without oxygen in the microscope, soot combustion was not observed. Then, a low oxygen partial pressure was gradually introduced at high temperature and the soot combustion process was *in-situ* observed. Numerous video sequences were recorded at a moderate resolution of about 1 nm (see figure 1). At 500°C under 2 mbar of oxygen, and 550°C under 3 mbar of oxygen, it is evidenced that the soot particles are consumed at the solid/solid interface. This result confirms that the YSZ bulk oxygen species are more reactive to oxidize soot than the gaseous species. Soot particles moved toward the YSZ grains and at the same time turned around the contact points with YSZ from which they are consumed. In addition, the combustion rate was found to be not constant with time, since the combustion reaction was strongly accelerated at the end of the process. Finally, in these operating conditions, the contact area between YSZ and the soot agglomerates remained unchanged as it was confirmed by High Resolution imaging after the heat treatment.

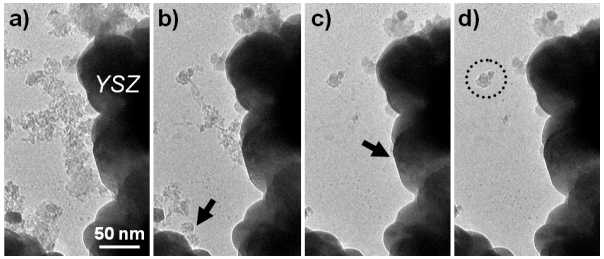

Figure 1: images extracted from a video sequence recorded under 3 mbar of O_2 at 550°C (ETEM 80 kV; time interval 40"). Arrows indicate YSZ contact points were the soot particles are consumed. Owing to the presence of a SiO_2 supporting film, residues of soot remain when no contact exists with any YSZ particle (circle in d).

Significance

These in-situ 'ETEM' observations confirm that bulk YSZ oxygens are the active species for soot oxidation at the soot/YSZ interface.

Acknowledgements

We acknowledge the CLYM (Centre Lyonnais de Microscopie, www.clym.fr) for its guidance in the Ly-EtTEM project which was financially supported by the CNRS, the Région Rhône-Alpes, the 'GrandLyon' and the French Ministry of Research and Higher Education. The authors are grateful to the ANR (Agence National de la Recherche) for funding "PIREP2" project (N° ANR-2010-VPTT 006-01) and ADEME (Agence de l'Environnement et de la Maîtrise de l'Energie) for the PhD grants of E. Obeid and A. Serve.

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