

Environmental TEM investigation of the mechanism of soot combustion by Ag supported catalysts

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1. INTRODUCTION

During the last few decades, Diesel engines have been generalized for a large number of vehicles over the whole world. In Europe, Diesel car emissions are restricted since 1993 by the EURO emissions standard, the last edition of which, Euro 6, limits Particulate Matter (PM) emissions to 4.5 mg/km and introduces a limitation in number: 6.10^{11} particles/km. To comply with these emissions standards since Euro 4, a PM exhaust treatment device has become necessary and Diesel Particle Filters (DPF) have been proven to be a really efficient way to diminish PM emissions [3]. However this system requires periodic regeneration phases during which the soot trapped in the filter is burnt. The soot ignition, thus the regeneration starts when a sufficient temperature is reached, generally over 600°C. In order to lower the regeneration temperature and thus limits the fuel over-consumption, various catalysts are used which aim at promoting the soot combustion: among them, we have recently studied yttria-stabilized zirconia (YSZ) catalysts [2,3]. Contrary to other oxides presenting RedOx properties (such as CeO₂), the catalytic activity of YSZ is thought to be due to its ability to conduct oxygen ions (especially in the cubic fluorite structure when stabilized with yttria). A fuel-cell type electrochemical process has been proposed to explain how YSZ oxidizes soot: the soot acts both as reactant and electronic conductor, consuming oxygen from the YSZ lattice and feeding electrons from an anode (the contact point between the soot and an YSZ particle) to a cathode (the gas phase in contact with the catalyst) [2]. The efficiency of the soot consumption is then controlled by the quality of the soot/catalyst contacts. In this context, the oxidation of real soot on YSZ particles was directly observed in Environmental Transmission Electron Microscopy (ETEM) in presence of oxygen up to 550°C; these experiments have unambiguously pointed out the importance of contacts between the soot particles and the catalyst [3]. To go further, the present investigation deals with the incorporation of silver NPs onto the YSZ powder to improve its efficiency. It is known that the combustion of soot is promoted by the presence of silver over various oxide-based catalyst supports [4], but the exact role of silver (and possibly silver oxide formation) was not accurately established since the microstructural evolution of the supported NPs was not *in situ* followed but only post-mortem observed in conventional TEM. Thus the present ETEM study was conducted in order to directly evidence the role of Ag NPs.

2. RESULTS

Ag NPs were dispersed on YSZ (8 mole%, from Tosoh) by wetness impregnation of silver nitrate (Alfa Aesar, 99.9%) and calcined at 700°C for 4 hours. The obtained catalysts with a Ag loading of 1 wt.% were characterized by several techniques: XRD, SEM, TEM, BET and Laser diffraction (for measuring the agglomerate size). Soot oxidation was carried out using a mixture of carbon black (Printex U) and catalyst in tight and loose contact conditions. Temperature-Programmed Oxidation (TPO) experiments were performed by heating the mixture under different oxygen partial pressures; TPR (TP Reduction) analysis and XPS were also performed to quantify the level of Ag oxide. ¹⁸O₂ TPO and isothermal exchanges enabled the identification of the origin of the active oxygen species involved in soot oxidation.

Environmental TEM experiments were conducted in the Ly-EtTEM, a last generation ETEM (TITAN 80-300 kV from FEITM). Mixtures of soot and Ag/YSZ catalyst powders were dispersed on TEM Cu grids covered with a SiO_x supporting layer (exhibiting a good resistance to oxidation). A Gatan Inconel heating holder was used to heat the grids up to 600°C under an oxygen partial pressure up to 10 mbar. Dedicated tests with and without gas and with the electron beam 'on' or 'off' were performed in temperature to ascertain that observed phenomena were at least not uniquely due to electron irradiation effects. Observations were performed at 300 kV and appeared qualitatively similar to those performed at 80 kV [3]. TPO experiments show that 1% Ag/YSZ

displays far better performance than YSZ with CO₂ selectivity higher than 95%. The catalytic performance was found to increase with the oxygen partial pressure. ¹⁸O experiments confirm the crucial role of YSZ bulk oxygen species in the soot oxidation mechanism, even in presence of Ag.

Movies recorded during ETEM experiments show Ag NPs tunneling through the soot and consuming it (Fig. 2). This result is related to a trench channeling mechanism previously identified (for example [5]) and based on the dissociation of O₂ molecules at the surface of the Ag NPs, and consecutive gasification of the soot into CO₂. The silver NPs appear to adopt the shape of the soot beads and spectacularly deform to cover the soot particulate surface and keep a tight contact with them. This demonstrates directly the high mobility of Ag NPs in contact with soot. Further representative observations will be reported, including sintering of Ag NPs, and even their possible evaporation when they enter in contact with the YSZ support after all the soot in contact with the oxide particles has been consumed.

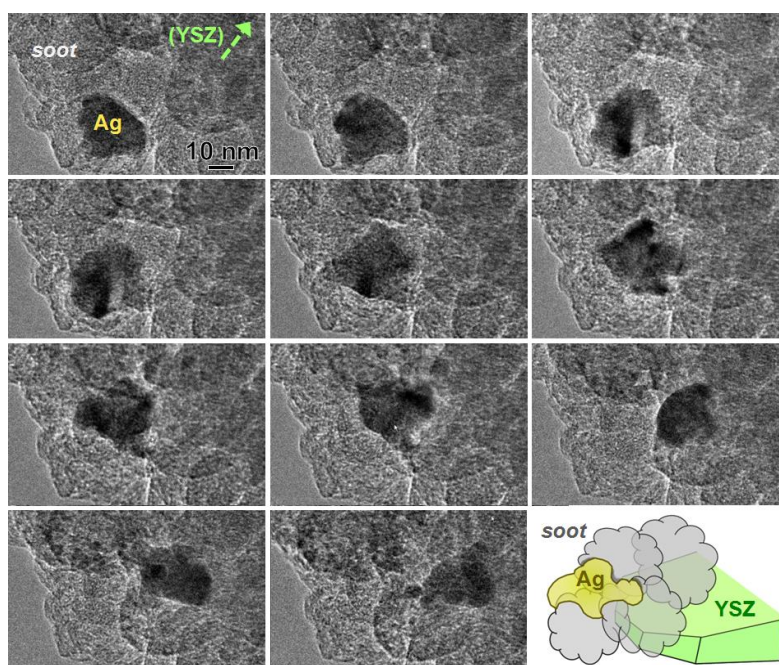


Figure 1. 300 kV ETEM observations of 1% Ag-YSZ + soot mixture under 495°C, 0.5 mbar of O₂ pressure: frames extracted every 3" from a video of about 30" (the sketch on the bottom right illustrates how the Ag NP followed in the movie deforms to adapt its shape to the topography of the soot particles).

3. CONCLUSION

The mechanism of soot combustion on Ag/YSZ catalyst have been investigated under DPF exhaust conditions with different experimental methods, including ETEM in situ observations at high temperature under oxygen partial pressure. Ag/YSZ catalysts display remarkable performances. Isotopic exchanges with labeled oxygen, ¹⁸O₂, confirm the crucial role of YSZ bulk oxygen species whereas ETEM results underline the fast mobility of Ag NPs [6].

REFERENCES

- [1] B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, *Catal. Rev.* **43** (2001) 489.
- [2] E. Obeid, L. Lizarraga, M.N. Tsampas, A. Cordier, A. Boréave, M.C. Steil, G. Blanchard, K. Pajot, P. Vernoux, *J. Catal.* **309** (2014) 87.
- [3] A. Serve, T. Epicier, M. Aouine, F. J. Cadete Santos Aires, E. Obeid, M. Tsampas, K. Pajot, P. Vernoux, to appear in *Appl. Catal. A.*, (2014).
- [4] E. Aneggi, J. Llorca, C. de Leitenburg, G. Dolcetti, A. Trovarelli, *Appl. Catal. B* **91** (2009) 489.
- [5] N. Severin, S. Kirstein, I.M. Sokolov, J.P. Rabe, *NanoLetters* **9** 1 (2009) 457-461.
- [6] The authors are grateful to ADEME (Agence de l'Environnement et de la Maîtrise de l'Energie) for the PhD grant of A.S. The CLYM (Consortium Lyon - St-Etienne de Microscopie, www.clym.fr) is acknowledged 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.