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Impact of the support on the catalytic activity of Ag nanoparticles for soot combustion

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This study investigates the catalytic activity for soot combustion of Ag nanoparticles dispersed on various supports showing different redox properties. Temperature programmed soot oxidation and isotopic exchange experiments were performed to assess the impact of the soot/catalyst contact, the oxygen partial pressure and the ageing toward activity. Three different contact modes have been used to clearly highlight the catalytic performances: loose, tight and supertight. Whatever the support, in both loose and tight contact modes, the catalytic performances are linked with the Ag surface concentration which was found to be high on zirconia-based catalysts and low on ceria-zirconia. The ignition of the soot combustion process occurs on Ag nanoparticles except for catalysts supported on Ytria-Stabilized Zirconia (YSZ), a pure oxygen ionic conductor, where Ag nanoparticles only promote the run-away of the reaction at higher temperatures. Catalysts based on SiO₂, ZrO₂ and YSZ exhibit a remarkable hydrothermal stability as performances in tight contact mode are fairly similar after the hydrothermal ageing.

1. Introduction

Particulate Matter (PM) emission abatement for passenger Diesel vehicles has become more and more stringent over the past years. In 2009, newly implemented Euro 5 standards lead to Diesel Particle Filter (DPF) becoming widespread to reduce PM emissions. DPF proved to be an efficient way to trap soot particles in the exhaust, the main drawback being the necessity to regenerate the filter regularly as soot collection slowly obstructs the filter, increasing the pressure drop. As temperature in the DPF is too low for oxidizing soot, fuel post-injections are commonly used to regenerate DPF regeneration. Post-injected fuel is oxidized in the Diesel Oxidation Catalyst (DOC), enhancing the temperature up to 600 °C in the DPF due to the exothermicity of the oxidation reactions, thus allowing soot oxidation. This strategy causes a fuel overconsumption which is detrimental to the overall CO₂ emission assessment of Diesel vehicles.

The aim of this study is to develop an active catalyst for the DPF regeneration at low temperature using only oxygen as an oxidant. Ceria oxides are good candidates due to their redox properties: surface oxygen vacancies can generate active oxygen species such as O₂⁻ and O⁻ [1–3]. Perovskites have been also reported to be efficient through the

involvement of weakly chemisorbed surface oxygen species as well as bulk oxygen species, who can migrate toward the oxidation site thanks to the ionic conductivity [4–7]. We have also shown that Ytria-Stabilized Zirconia (YSZ), a well-known pure oxygen ionic conductor, can oxidize soot [8–10] with lattice oxygen active species with a concomitant gaseous oxygen replenishment into the lattice. Soot oxidation observed by E-TEM (Environmental Transmission Electronic Microscope) displayed that the reaction occurred at the soot/YSZ interface [8]. Using isotopic experiments, we have proposed a fuel-cell type electrochemical mechanism to explain the ignition of the soot oxidation on YSZ. The soot could be electrochemically oxidized with ionic O²⁻ species at the soot/YSZ interface whereas YSZ is replenished via gas-phase oxygen electrochemical reduction at the triple phase boundary (tpb) gas/soot/YSZ. As in fuel cells, the electromotive force of this process is the gradient of oxygen concentration between the tpb and the soot/YSZ interface. This process is limited by the kinetic of the incorporation of gaseous oxygen into YSZ. Recently [11], we demonstrated that the presence of silver nanoparticles (Ag NPs) over YSZ enhanced soot oxidation performances in both loose and tight contact modes. Ag NPs were shown to boost soot oxidation activity by promoting the dissociative adsorption and lattice integration of gaseous

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oxygen into the YSZ support. Ag/YSZ catalysts have shown promising catalytic performances for low Ag loadings in the range 1–2 wt.%.

This paper describes catalytic activity for soot combustion of Ag NPs dispersed on various supports showing different redox properties: SiO₂ as a non-redox oxide with a large specific surface area, ceria-zirconia as a reference redox material [12,13], YSZ as a pure oxygen ionic conductor and non-doped ZrO₂ for comparison. This study mainly focused on the hydrothermal stability of the Ag supported catalysts. In addition, two kinds of YSZ powders were used with different surface properties and grain sizes. Various characterization techniques (XPS, TEM, UV-vis, H₂-TPR) were carried out to investigate the Ag NPs oxidation state, shape and dispersion. Temperature programmed soot oxidation were performed to assess the impact of the soot/catalyst contact, the oxygen partial pressure and the ageing toward activity. Three different contact modes have been used to clearly highlight the catalytic performances of the catalysts: loose, tight and supertight. The latter has been obtained from propene cracking which can produce a nanometric carbon film onto the catalyst surface. Finally, Temperature-Programmed Isotopic Exchange experiments were performed to get further insight into the catalytic mechanism.

2. Experimental

2.1. Catalysts preparation and characterizations

Supports used were commercial YSZ (8% mol yttria) and non-doped zirconia (ZrO₂) purchased from Tosoh company, YSZb (also containing 8% mol yttria) furnished by Céramiques Techniques Industrielles, SiO₂ from Sigma-Aldrich and ceria-zirconia (Ce_{0.7}Zr_{0.3}O₂) supplied by Solvay company. These materials were impregnated with a silver nitrate aqueous solution obtained by dissolution of AgNO₃ (Sigma Aldrich, purity 99%) to achieve 1,3 wt% Ag loading. Indeed, according to reference [11], the optimal Ag loading to reach the highest catalytic performance was in the range 1–2 wt%. Samples were dried overnight at 100 °C and finally annealed at 700 °C for 4 h in flowing air [11]. Table 1 summarizes the list of the as-prepared Ag supported catalysts (denoted as calcined) and their nomenclature. Hydrothermal ageing was carried out at 900 °C for 10 h in flowing air containing 10 vol.% H₂O (denominated aged in Table 1). Silver loading was determined by ICP-OES using a Horiba Jobin Yvon Activa spectrometer. XRD diffractograms were recorded with a Bruker D8 Advance A25 diffractometer using Cu K α radiation. Specific Surface Areas (SSA) were measured from N₂ adsorption at –196 °C (BET method), using a Tristar Surface Area and Porosity Measurement apparatus from Micromeritics. The BJH method was used to determine the pore size distribution. Silver and support average crystallites size were calculated using the Scherrer equation when corresponding peaks intensities were high enough to obtain accurate data. Samples d50 (grain diameter at half distribution) was measured using a Laser diffraction spectroscopy.

XPS spectra were recorded for each catalysts on an AXIS Ultra DLD from Kratos Analytical using a monochromatized Al X-ray source (h ν = 1486,6 eV). Sample were pretreated at 200 °C in He before

measurements to clean the surface, scanning energy was 40 eV for every region. Peaks were referenced using C1S peak of carbon (BE = 284.6 eV).

Calcined and aged samples were observed by TEM using a JEOL 2010 microscope. Acceleration voltage was 200 kV with a 0.2 nm resolution. Samples were previously dispersed in ethanol using an ultrasound bath and then deposited on a copper mesh. Ag NPs diameter distribution was estimated over an average of 20 micrographs per catalyst by measuring at least 150 Ag NPs.

UV-Vis analysis were performed on calcined samples at room temperature in ambient air using a Lambda 950 UV-vis spectrophotometer (Perkin Elmer) equipped with an integrating sphere detector. Reflectance was measured and converted to absorbance using a Kubelka-Munk function. Blanks were performed prior to each experiments by using a Spectralon sample.

Temperature programmed reduction experiments were carried out over all calcined catalysts. 200 mg of catalyst were deposited in a U shaped quartz reactor. A reactive mixture of 1% H₂/He was introduced at 6 L.h^{–1} and the reactor was heated with a heating ramp of 10 °C/min rate up to 450 °C. H₂ (*m/z* = 2) signal was recorded using an Inficon quadrupole mass spectrometer. Signal calibration was performed prior to and after every experiments to assess the potential signal deviation of the MS over time.

2.2. Catalytic performances measurements

Soot oxidation activity was measured by TPO (Temperature Programmed Oxidation) of a mixture of a model soot (Printex U) and the catalyst under 5% O₂/He with an overall flow of 100 mL/min. Temperature ramp was 10 °C/min from room temperature up to 750 °C. Two contact modes between model soot particles and catalyst grains were investigated. The ‘tight’ contact mode was obtained by grinding the catalyst and the soot together in a ball-mortar containing two zirconia balls of 5 mm diameter at 15 Hz for 2 min. ‘Loose’ contact mixture was obtained by only mixing the two elements with a spatula for 5 min. ‘Tight’ contact mode leads to improved contact between soot and catalyst and is generally used to assess the intrinsic activity of the catalyst toward soot oxidation. The ‘Loose contact’ mode is considered to be more representative of the poor contact quality obtained between a catalyst wash-coat and soot particles trapped in a catalyzed-DPF [14, 15]. TPO experiments reproducibility was checked by conducting experiments twice. Soot to catalyst mass ratio was ¼, 25 mg of the soot/-catalyst mixture was introduced in a U-tube quartz reactor. Outlet gases (CO and CO₂) were analyzed by a micro-chromatograph from SRA. In addition, the CO₂ concentration was on-line measured with a Horiba IR analyzer. Soot to gas conversion was obtained by integration of the molar production rate of CO and CO₂ with respect to time during soot oxidation experiments, followed by normalization with respect to the total amount of soot initially present in the reactor. Soot to gas conversion allowed for determination of T₁₀ and T₅₀ values, corresponding respectively to temperatures at which 10% and 50% of the soot is converted to gas.

2.3. Propene cracking

To get further insight into the intrinsic activity of the catalyst to oxidize carbon, a nanometric carbon layer was *in-situ* deposited on the catalyst surface by propene cracking (1). 200 mg of each sample was introduced in U-shaped quartz reactor and reduced at 500 °C under pure hydrogen during 30 min to limit the reaction between propene and adsorbed oxygen species. Then, samples were heated up to 600 °C under He and a mixture of propene in helium (8000 ppm) was introduced for 30 min. Reactor was then flushed with He and cooled down rapidly to room temperature. TPO was then performed in 5% O₂/He at 10 °C/min up to 600 °C. Deposited carbon quantity was estimated from CO and CO₂ produced during the TPO. The production of hydrogen at 600 °C as well as the concomitant consumption of propene were checked by using a

Table 1

Support grain size, silver loadings and average silver particle crystallite size obtained by the Scherrer equation after calcination at 700 °C and hydrothermal ageing.

Catalysts	d50 (μm)	Ag loading (%wt)		Ag loss (%)	Average Ag NPs crystallite size (nm)	
		Calcined	Aged		Calcined	Aged
1Ag/YSZ	68	1.1	0.8	27	31 ± 6	48 ± 4
1Ag/YSZb	0.3	1.2	1.1	8	36 ± 6	52 ± 6
1Ag/ZrO ₂	68	1.1	0.9	18	–	61 ± 6
1Ag/SiO ₂	0.3	1.3	1.2	7	16 ± 2	36 ± 3
1Ag/CZ	6	1	0.6	40	–	–

mass spectrometer (HIDEN, HPR20). No oxidation products such as CO or CO₂ were detected for all samples with the exception of CZ where considerable amounts of CO were produced during the first minutes. Small amounts of methane were also detected during the first minutes of propene cracking.

A second streak of tests was then carried out with a propene cracking time adjusted for each oxide support in order to obtain a deposition in the range 30–40 μmoles of carbon. Cracking time ranged from 10 to 30 min depending on the sample.

2.4. Temperature-programmed Isotopic exchange (TPIE)

TPIE experiments were performed over each calcined catalysts to investigate the impact of the support on the rate of oxygen exchange. A reactive mixture with labeled oxygen, 1%¹⁸O₂/He, was obtained by dilution of pure marked O₂ (97.1% ¹⁸O, 0.8%¹⁷O, 2.1%¹⁶O) obtained from EURISOTOP in He. A flow of 75 ml/min was introduced in a quartz reactor containing 200 mg of catalyst. Heating rate was 5 °C/min from room temperature to 700 °C. A Hidden quadrupole mass spectrometer was used to analyze the outlet gases, signals *m/z* followed were 32, 34 and 36. Signal calibration was performed by using a 1%¹⁶O₂/He (99.99% purity) calibration bottle provided by Linde. A blank experiment in presence of both 1% of ¹⁶O₂ and ¹⁸O₂ in the reactor was performed without any catalyst to check that gaseous homoexchange in the gas phase does not take place until 700 °C.

Molar fractions of oxygen isotopomers were calculated by using (2):

$$F_{32} = C_{32} / (C_{32} + C_{34} + C_{36}) \quad (2)$$

where *F* is an isotopomer molar fraction and *C*₃₂, *C*₃₄ and *C*₃₆ are the respective concentrations of the three O₂ isotopomers detected during the experiment. The ¹⁸O₂ consumption rate (*R*_{consumption, T}) and the production rate (*R*_{production, T}) of normal oxygen (¹⁶O₂) at a given temperature *T* was calculated using (3) and (4) equations.

$$R_{\text{consumption, T}} = F \cdot (F_{36 \text{ in, T}} - F_{36 \text{ out, T}}) / V_m \quad (3)$$

$$R_{\text{production, T}} = F \cdot (F_{32 \text{ out, T}}) / V_m \quad (4)$$

where *F* (L/s) is the total flow rate, *F*_{36 in, T} is the oxygen fraction at the reactor's inlet, *F*_{36 out, T} and *F*_{32 out, T} are the ¹⁸O₂ and ¹⁶O₂ fractions measured at the reactor's outlet at temperature *T*, and *V*_m is the molar volume. Without production of ¹⁶O¹⁸O in the gas phase, the surface oxygen exchange rate corresponds to the consumption rate of ¹⁸O₂ if this latter is equal to the production rate of ¹⁶O₂.

3. Results and discussion

3.1. Characterizations

3.1.1. Texture characterizations

The support granulometry, SSA, pores size and pore volumes of the different catalysts are summarized in Table 2. YSZ and ZrO₂, both

Table 2
Textural properties of catalysts after calcination at 700 °C and hydrothermal ageing.

Catalysts	Specific surface area (m ² /g)		Porous volume (cm ³ /g)		Pores size (nm)	
	Calcined	Aged	Calcined	Aged	Calcined	Aged
1Ag/YSZ	12	7	0.04	0.01	2.3/30	7
1Ag/YSZb	6	4	0.02	0.01	12	7
1Ag/ZrO ₂	12	6	0.06	0.01	2.3/40	7
1Ag/SiO ₂	180	135	1.53	1.18	29	33
1Ag/CZ	71	14	0.21	0.11	2.2/9	2.3/40

manufactured by Tosoh by atomization method, display large spherical agglomerates with diameters in the range 20–160 μm and a median diameter *d*₅₀ of 68 μm . YSZb and SiO₂ powders contain randomly shaped agglomerates, smaller than 3 μm with a median diameter of 0.3 μm . CZ displays spherical agglomerates of average diameter with a *d*₅₀ of 6 μm .

Both SiO₂ and CZ based catalysts exhibit higher SSA values, (180 and 71 m²/g, respectively) compared to zirconia based catalysts. Similarly, 1Ag/SiO₂ displays the highest pore volume followed by 1Ag/CZ. SSA and pore volume of 1Ag/YSZb are the lowest among studied catalysts. All Ag-supported catalysts are mesoporous. The pore size distribution of 1Ag/YSZ, 1Ag/ZrO₂ and 1Ag/CZ is bimodal, showing small pores in the range 2.2–2.5 nm alongside with larger ones, of around 30–40 nm for zirconia based support and 9 nm for 1Ag/CZ. On the other hand, Ag/YSZb only contains one medium pore size of around 12 nm. The sample 1Ag/SiO₂ displays the biggest medium pore size of 29 nm.

As expected, after hydrothermal ageing, we notice a general drop of samples SSA and pore volume (Table 2). 1Ag/CZ is the most impacted catalyst with SSA dropping from 71 to 14 m²/g and pore volume from 0.21 to 0.11 cm³/g. Larger pores of 40 nm are detected which might result from initial 9 nm pores crumbling. The SSA and the pore volume of 1Ag/SiO₂ are reduced but still remain one order of magnitude higher than those of other catalysts. The texture of 1Ag/YSZ and 1Ag/ZrO₂ follows similar evolution resulting in a reduced SSA and a diminution of both the volume and the size of the pores. The pore size distribution becomes unimodal upon ageing with a mean pore diameter of around 7 nm. Interesting to note that 1Ag/YSZb exhibits the best thermal stability.

3.1.2. Silver loading on calcined and aged catalysts

Calcined catalysts contain a silver loading ranging from 1 to 1.3 wt %, while the theoretical one was 1.3 wt%. In addition, after hydrothermal ageing, we observed a drop in the Ag content, due to the high vapor pressure of Ag (melting point at 961 °C). The Ag loss after ageing (Table 1) strongly depends on the nature of the support. The Ag loss is small, only 7 and 8% on SiO₂ and YSZb, respectively whereas it is significant on YSZ, ZrO₂ and CZ. Interestingly, the percentage of Ag loss follows the same rank than the Ag loading in the calcined catalysts (Table 1). This indicates that Ag loss most probably also takes place during the calcination step at 700 °C and is particularly pronounced on CZ, ZrO₂ on YSZ. This explains the lower Ag loading measured on these supports after calcination. For instance, on CZ, the Ag loading is only 1 wt%, suggesting that almost 23% of the Ag NPs sublimated during the calcination step at 700 °C. These results are in good agreement with those reported by Sun et al. [16] who observed, with TEM, the sublimation of Ag NPs supported on silica from 600 °C. TEM analysis also reveals that this phenomenon is more pronounced and faster on smallest Ag NPs located on the surface with respect to those anchored inside pores. This could indicate that Ag NPs are mainly located in the pores of YSZb and SiO₂ in good agreement with the absence of small 2 nm size pores on these two supports contrary to all other oxides.

3.1.3. Structure characterizations

XRD analysis were carried out to check the stability of the support structure after the hydrothermal ageing and to estimate the crystallite size of Ag NPs. Both 1Ag/YSZ and 1Ag/YSZd can be indexed as a pure fluorite cubic phase and 1Ag/CZ as a cubic phase. 1Ag/ZrO₂ displays a predominant monoclinic phase (Fig. 1). No modification of supports structure was detected after ageing. After hydrothermal ageing, the sintering of the support is observed mostly over 1Ag/CZ as diffraction peaks become sharper and corresponding intensities increase in good agreement with SSA measurements. As expected, SiO₂ is amorphous.

Whatever the nature of the support, only metallic silver has been detected on the diffractograms in good agreement with previous studies over Ag NPs supported on ZrO₂, CeO₂, Al₂O₃ and SiO₂ [17–21]. Nevertheless, intensities of the metallic silver diffraction peaks (38.1°, 38.4°, 39.2°, 40.2°, 44.5°, 47.5°, 56.5°, 57.5°, 60.1°, 60.4°, 60.6°, 60.8°, 60.9°, 61.0°, 61.1°, 61.2°, 61.3°, 61.4°, 61.5°, 61.6°, 61.7°, 61.8°, 61.9°, 62.0°, 62.1°, 62.2°, 62.3°, 62.4°, 62.5°, 62.6°, 62.7°, 62.8°, 62.9°, 63.0°, 63.1°, 63.2°, 63.3°, 63.4°, 63.5°, 63.6°, 63.7°, 63.8°, 63.9°, 64.0°, 64.1°, 64.2°, 64.3°, 64.4°, 64.5°, 64.6°, 64.7°, 64.8°, 64.9°, 65.0°, 65.1°, 65.2°, 65.3°, 65.4°, 65.5°, 65.6°, 65.7°, 65.8°, 65.9°, 66.0°, 66.1°, 66.2°, 66.3°, 66.4°, 66.5°, 66.6°, 66.7°, 66.8°, 66.9°, 67.0°, 67.1°, 67.2°, 67.3°, 67.4°, 67.5°, 67.6°, 67.7°, 67.8°, 67.9°, 68.0°, 68.1°, 68.2°, 68.3°, 68.4°, 68.5°, 68.6°, 68.7°, 68.8°, 68.9°, 69.0°, 69.1°, 69.2°, 69.3°, 69.4°, 69.5°, 69.6°, 69.7°, 69.8°, 69.9°, 70.0°, 70.1°, 70.2°, 70.3°, 70.4°, 70.5°, 70.6°, 70.7°, 70.8°, 70.9°, 71.0°, 71.1°, 71.2°, 71.3°, 71.4°, 71.5°, 71.6°, 71.7°, 71.8°, 71.9°, 72.0°, 72.1°, 72.2°, 72.3°, 72.4°, 72.5°, 72.6°, 72.7°, 72.8°, 72.9°, 73.0°, 73.1°, 73.2°, 73.3°, 73.4°, 73.5°, 73.6°, 73.7°, 73.8°, 73.9°, 74.0°, 74.1°, 74.2°, 74.3°, 74.4°, 74.5°, 74.6°, 74.7°, 74.8°, 74.9°, 75.0°, 75.1°, 75.2°, 75.3°, 75.4°, 75.5°, 75.6°, 75.7°, 75.8°, 75.9°, 76.0°, 76.1°, 76.2°, 76.3°, 76.4°, 76.5°, 76.6°, 76.7°, 76.8°, 76.9°, 77.0°, 77.1°, 77.2°, 77.3°, 77.4°, 77.5°, 77.6°, 77.7°, 77.8°, 77.9°, 78.0°, 78.1°, 78.2°, 78.3°, 78.4°, 78.5°, 78.6°, 78.7°, 78.8°, 78.9°, 79.0°, 79.1°, 79.2°, 79.3°, 79.4°, 79.5°, 79.6°, 79.7°, 79.8°, 79.9°, 80.0°, 80.1°, 80.2°, 80.3°, 80.4°, 80.5°, 80.6°, 80.7°, 80.8°, 80.9°, 81.0°, 81.1°, 81.2°, 81.3°, 81.4°, 81.5°, 81.6°, 81.7°, 81.8°, 81.9°, 82.0°, 82.1°, 82.2°, 82.3°, 82.4°, 82.5°, 82.6°, 82.7°, 82.8°, 82.9°, 83.0°, 83.1°, 83.2°, 83.3°, 83.4°, 83.5°, 83.6°, 83.7°, 83.8°, 83.9°, 84.0°, 84.1°, 84.2°, 84.3°, 84.4°, 84.5°, 84.6°, 84.7°, 84.8°, 84.9°, 85.0°, 85.1°, 85.2°, 85.3°, 85.4°, 85.5°, 85.6°, 85.7°, 85.8°, 85.9°, 86.0°, 86.1°, 86.2°, 86.3°, 86.4°, 86.5°, 86.6°, 86.7°, 86.8°, 86.9°, 87.0°, 87.1°, 87.2°, 87.3°, 87.4°, 87.5°, 87.6°, 87.7°, 87.8°, 87.9°, 88.0°, 88.1°, 88.2°, 88.3°, 88.4°, 88.5°, 88.6°, 88.7°, 88.8°, 88.9°, 89.0°, 89.1°, 89.2°, 89.3°, 89.4°, 89.5°, 89.6°, 89.7°, 89.8°, 89.9°, 90.0°, 90.1°, 90.2°, 90.3°, 90.4°, 90.5°, 90.6°, 90.7°, 90.8°, 90.9°, 91.0°, 91.1°, 91.2°, 91.3°, 91.4°, 91.5°, 91.6°, 91.7°, 91.8°, 91.9°, 92.0°, 92.1°, 92.2°, 92.3°, 92.4°, 92.5°, 92.6°, 92.7°, 92.8°, 92.9°, 93.0°, 93.1°, 93.2°, 93.3°, 93.4°, 93.5°, 93.6°, 93.7°, 93.8°, 93.9°, 94.0°, 94.1°, 94.2°, 94.3°, 94.4°, 94.5°, 94.6°, 94.7°, 94.8°, 94.9°, 95.0°, 95.1°, 95.2°, 95.3°, 95.4°, 95.5°, 95.6°, 95.7°, 95.8°, 95.9°, 96.0°, 96.1°, 96.2°, 96.3°, 96.4°, 96.5°, 96.6°, 96.7°, 96.8°, 96.9°, 97.0°, 97.1°, 97.2°, 97.3°, 97.4°, 97.5°, 97.6°, 97.7°, 97.8°, 97.9°, 98.0°, 98.1°, 98.2°, 98.3°, 98.4°, 98.5°, 98.6°, 98.7°, 98.8°, 98.9°, 99.0°, 99.1°, 99.2°, 99.3°, 99.4°, 99.5°, 99.6°, 99.7°, 99.8°, 99.9°, 100.0°).

Fig. 1. Silver supported catalysts diffractograms, a) after calcination, b) after hydrothermal ageing.

44.3° and 64.5°, JCPDS # 04-0783) are low for all catalysts. Furthermore, no peak corresponding to Ag° can be detected on calcined 1Ag/CZ. This could indicate a high Ag dispersion on CZ. On calcined 1Ag/ZrO₂, the diffraction peak at 38.1° of Ag° is hidden by the support diffraction pattern. Therefore, intensities of the Ag° diffraction peaks only allow an estimation of Ag NPs crystallite size when dispersed on YSZ, YSZb and SiO₂ (Table 1). Average Ag NPs crystallite sizes are similar over both kinds of YSZ, of around 30 nm. As expected from its much higher SSA, 1Ag/SiO₂ displays smaller Ag NPs crystallite size (16 nm). Smallest sizes between 10 and 20 nm are reported in the literature data [20,22,23] from XRD analysis but this can be explained by lower calcination temperatures (500 °C or 600 °C). After hydrothermal treatment, the XRD peaks of Ag° are detectable over all catalysts.

Peaks are high enough to perform an estimation of the Ag NPs size from the Scherrer calculation except for 1Ag/CZ. This could be related to the high silver loss (Table 1). Sintering is observed for 1Ag/YSZ and 1Ag/YSZb with an average crystallite size increased by 50% and reaching 50 nm. Slightly higher value is obtained for 1Ag/ZrO₂ with 61 nm. Sintering over 1Ag/SiO₂ appears to be more severe with an average silver crystallite size doubled after ageing (36 nm). Sintering starting from 400 °C was reported by Sun et al. for Ag NPs supported over SiO₂ [16]. Moulijn et al. [24] reported that metal particles mobility can be observed at the Hüttig temperature corresponding to $0.3T_{\text{melting}}$. At this temperature, which corresponds to 320 °C in the case of metallic silver, atoms located at the edge and defect of the NPs become mobiles. Bulk mobility is reached at the Tamman temperature corresponding to $0.5T_{\text{melting}}$ (480 °C), leading to coalescence phenomena.

3.1.4. TEM characterizations

TEM observations were performed over all catalysts, after calcination and ageing (Fig. 2). Contrast between support and Ag NPs is rather weak for zirconia-based catalysts and for 1Ag/CZ. This is related to atomic numbers of Ag (47) and Zr (40) being similar. Such low contrast results in large Ag NPs being confounded with supports grains. Thus, calculated size distributions might mainly focus on the smaller and surface particles (< 20 nm). Furthermore, in the case of 1Ag/CZ, Ag NPs are too small to be easily discernable from the support and no clear conclusion can be drawn on size and shape of Ag NPs on CZ. TEM observations on the other samples indicate that Ag NPs are round-shaped. Ag NPs size distribution is wide whatever the calcined catalyst, ranging from 3 nm to more than 30 nm (Fig. 3a). 1Ag/YSZ and 1Ag/ZrO₂ display slightly more numerous smaller particles (distribution centered on 8 nm), while 1Ag/YSZb and 1Ag/SiO₂ show a distribution centered on 10 nm, which extends to larger diameters. This size differs from the one obtained in XRD on zirconia-based catalysts (Table 1), which is around 35 nm. This can be explained by XRD being a volumetric analysis, sensitive to the overall amount of silver, while TEM observations only focus on the discernible surface small particles. Similar difference between XRD analysis and TEM observations was already reported in the literature by Kundakovic and Flytzani-Stephanopoulos for silver-supported zirconia calcined at 650 °C [19]. Authors concluded on the coexistence of numerous smaller particles (in the 5 nm range) along with bigger ones (>30 nm). Similar conclusion can be drawn from XRD and TEM data and one can assume that Ag NPs on zirconia-based catalysts display a bimodal size distribution centered on 8–10 nm for the smaller ones and on 40 nm for the largest. Over 1Ag/SiO₂ where contrast does not impact Ag NPs detection, XRD and TEM observations match more

Fig. 2. TEM micrographs of a) 1Ag/YSZ, b) aged 1Ag/YSZ, c) 1Ag/YSZb, d) aged 1Ag/YSZb, e) 1Ag/ZrO₂, f) aged 1Ag/ZrO₂, g) 1Ag/CZ, h) aged 1Ag/CZ, i) 1Ag/SiO₂, j) aged 1Ag/SiO₂.

Fig. 3. Ag NPs diameter distribution observed by TEM, a) calcined catalysts, b) aged catalysts.

closely: 16 and 10 nm with XRD and TEM, respectively.

Upon ageing, all distributions are shifted toward largest sizes (Fig. 3b). Zirconia-based catalysts still contain Ag NPs smaller than 15 nm (accounting for 70% of the distribution). Bimodal distribution is maintained with diameters in the range 10–12 nm for small particles while bigger particles measured by XRD ranges from 50 to 60 nm for these samples. Ageing impact is mostly detectable over 1Ag/SiO₂ as Ag NPs are mainly larger than 30 nm (55% of the distribution) without any particles smaller than 14 nm. This result is in good agreement with XRD (Table 1).

3.1.5. Surface characterizations

Ratios between the surface, determined by XPS, and volume, measured by ICP, Ag atomic percentage give a good indication of the surface Ag concentration (Table 3). Zirconia-based catalysts exhibit a surface segregation of Ag at ratios are larger than 1 (Table 3). This trend is much more pronounced on YSZ and ZrO₂. This indicates that Ag NPs are mainly located on the surface. On the other hand, silver is slightly less present at the outer surface than over the whole volume on CZ, indicating that some Ag NPs might be present in the pores. Similarly, 1Ag/SiO₂ displays very low fraction of Ag on its surface in good accordance with its high pore volume. After ageing, the fraction of Ag NPs on the surface was found to be stable on YSZb whereas on YSZ it drops by a factor 2.5. Such results follow the same trend than the Ag loss, indicating that remaining Ag NPs on YSZ after ageing are mainly located in the pores. Similar correlation between Ag loss and Ag surface concentration diminution is observed for 1Ag/ZrO₂ upon ageing, even if on this support, a Ag surface segregation still exists. On SiO₂, the atomic

Table 3

XPS analysis of silver supported catalysts, silver and yttria atomic surface to volume ratio.

Catalysts	Silver surface to volume atomic ratio		Y/Zr surface to volume atomic ratio	
	calcined	aged	calcined	aged
1Ag/YSZ	1.57	0.62	1.5	1.6
1Ag/YSZb	1.30	1.27	1.3	1.6
1Ag/ZrO ₂	1.59	1.36	–	–
1Ag/SiO ₂	0.19	0.07	–	–
1Ag/CZ	0.89	1.37	–	–

fraction of Ag NPs on the surface becomes negligible after ageing, demonstrating that large Ag NPs observed by TEM are mainly covered by silica.

1Ag/CZ displays higher surface Ag atomic fraction upon ageing while its SSA, pore volume and Ag loading drastically drop. A hypothesis would be that Ag NPs contained within the pores are expelled during ageing and remain small, maintaining a good dispersion.

In the case of 1Ag/YSZ and 1Ag/YSZb, Y/Zr surface to volume atomic ratios have been extracted from XPS experiments. They represent the concentration gradient of yttrium between the surface and the bulk. Both 1Ag/YSZ and 1Ag/YSZb catalysts display a surface segregation of yttrium. Such effect has already been reported in the literature for Tosoh YSZ [11,25]. The surface yttrium segregation is more pronounced on YSZ. Therefore, different surface properties are expected between 1Ag/YSZ and 1Ag/YSZb. For instance, the surface oxygen vacancies concentration is supposed to be higher on YSZ than on YSZb, on the opposite of the concentration of acidic sites. Upon ageing, Y³⁺ segregation increases for both 1Ag/YSZ and 1Ag/YSZb, Y/Zr ratio reaches 1.6. This increase is more pronounced over 1Ag/YSZb (initial ratio of 1.3) than over 1Ag/YSZ (1.5), indicating a significant diffusion of yttrium on surface on YSZb during the hydrothermal treatment.

XPS analysis have also shown, for all Ag supported catalysts, that the Ag 3d_{5/2} binding energy peak is centered below 368 eV (Fig. S1), corresponding to Ag⁺ ions. As the average silver particle size range is 15–40 nm according to XRD data, one can assume that the top layer of the nanoparticles is mainly composed of silver oxides which are reduced during TPR but are not detected by XRD measurements.

3.1.6. UV-vis spectroscopy

UV-vis analysis were performed over bare supports and silver-supported catalysts in air at RT in 200–800 nm domain on the calcined catalysts (Fig. 4). Difference between the two series of spectra underlines the absorption bands relative to Ag NPs. UV spectra recorded on zirconia based catalysts evidence cationic Ag clusters (absorption band at 250 nm [18,19]) and metallic clusters and aggregates (bands at 320 nm and beyond 400 nm [30,34,18,19,26,27]). Absorption difference is stronger for 1Ag/YSZ and 1Ag/YSZb beyond 320 nm which would imply that metallic silver particles are more present than over 1Ag/ZrO₂. Similarly, Kundakovic and Flytzani-Stephanopoulos also reported the presence of both metallic silver and oxide silver (the latter possibly covering metallic silver) on silver-supported zirconia prepared by impregnation followed by calcination at 650 °C for 8 h [19].

The UV spectra difference between that of 1Ag/CZ and CZ clearly displays an intense absorption band at 200 nm, representative of isolated Ag⁺ ions [18,26]. A second absorption domain in the 360–460 nm range demonstrates the presence of metallic silver with metallic agglomerates. Presence of isolated Ag⁺ ions are in good agreement with the absence of silver peaks detected in XRD, which indicates a high

Fig. 4. UV-vis absorption difference between supports and silver-supported catalysts recorded in air at RT.

dispersion of silver.

Absorption bands at 250–300 nm and in the 340–450 nm range are detected over 1Ag/SiO₂. These indicate the presence of both cationic and metallic clusters and aggregates, as for zirconia-based catalysts. Corro et al. [18] have done similar UV–vis analysis over Ag/SiO₂ calcined at 450 °C for 6 h prior and after reduction in H₂ at 500 °C. They have shown that calcined Ag/SiO₂ mostly contained Ag⁺ isolated ions, while the reduction mostly formed metallic clusters. As our sample was calcined at much higher temperature (700 °C), one can expect that isolated Ag⁺ ions have coalesced, leading to bigger agglomerates, possibly displaying both metallic and oxide phases. This hypothesis correlates the average Ag NPs size detected by TEM and XRD: 10 and 16 nm respectively.

3.1.7. Reducibility of the Ag-supported catalysts

Reducibility of the calcined samples was investigated by running TPR (Fig. 5). Spectra display a H₂ consumption in a broad temperature range between 50 °C and 300 °C except for 1Ag/CZ due to the reduction of CZ from around 250 °C [28]. Various H₂ consumption peaks are observed at 75 °C, 140 °C and around 250 °C indicating that different reducible AgO_x species are present over the catalysts surface in good agreement with similar experiments reported in the literature for Ag supported on SiO₂ [29], Al₂O₃ [27], ZrO₂ [30] and CeO₂ [31,32]. Reduction peaks were associated with Ag₂O particles and well-dispersed Ag⁺ species or oxidized silver clusters. Reduction peaks in the temperature range 60–110 °C were obtained for a 10%Ag/CeO₂ catalyst calcined at 400 °C during reduction under 5% H₂/He [32]. First reduction peak was associated with AgO reduction to Ag₂O and second one corresponded to Ag₂O reduction to metallic Ag. The smaller the Ag₂O particles, the higher the reduction temperature. Therefore, the shifted reduction of 1Ag/CZ to higher temperatures compared to the other catalysts indicates that this sample contains smaller AgO_x NPs. Regarding the other catalysts, the wide temperature domain of the samples reduction as well as the presence of several overlapped peaks suggest that silver oxide is present at the catalyst surface under different forms and sizes, as already shown by UV–vis spectroscopy. The overall amount of H₂ consumption has been estimated by integrating the TPR spectra between room temperature and 300 °C. Samples 1Ag/YSZ, 1Ag/ZrO₂ and 1Ag/SiO₂ display similar H₂ consumption larger than that observed on 1Ag/YSZb. More interesting, the H₂/Ag molar ratio is 3 times lower on 1Ag/YSZb than on 1Ag/YSZ (Fig. 5, Table 4). This indicates that 1Ag/YSZb contains the lowest amount of silver oxide species while, on the opposite, YSZ seems to stabilize the largest amount of AgO_x. Ag NPs size distribution indicates that 1Ag/YSZ display smaller

Fig. 5. H₂ consumption rate with respect to temperature during TPR experiments under 1%H₂/He. blue: 1Ag/YSZ, red: 1Ag/YSZb, brown: 1Ag/SiO₂, purple: 1Ag/ZrO₂, green: 1Ag/CZ. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

Table 4

Consumed amounts of H₂ during TPR, ratio of consumed hydrogen by total amount of silver on the catalyst (*shoulder fitted by the dotted line).

Catalysts	n H ₂ consumed (μmol)	H ₂ /Ag total
1Ag/YSZ	14	0.46
1Ag/YSZb	5	0.16
1Ag/ZrO ₂	10	0.32
1Ag/SiO ₂	11	0.3
1Ag/CZ	3 ^a	0.11 ^a

^a Shoulder fitted by the dotted line in Fig. 4.

particles which are more prone to be oxidized, thus leading to higher amount of consumed H₂ during reduction. As observed in UV–vis and TEM, 1Ag/SiO₂ displays cationic silver clusters and Ag NPs of various sizes which would explain the overall H₂ consumption over a wide temperature range. Presence of well-dispersed Ag⁺ species over 1Ag/CZ was detected by UV-VIS analysis, reduction of such species corresponds to the H₂ consumption shoulder between 100 and 160 °C indicated by the dotted line in Fig. 5.

3.2. Temperature programmed isotopic exchange (TPIE)

To assess silver effect toward surface oxygen exchange, we performed TPIE experiments over all calcined catalysts. In presence of silver, oxygen exchange starts in the range 310–330 °C with the exception of 1Ag/SiO₂ where exchange begins from 450 °C (Fig. 6). Over zirconia-based bare supports, exchange starts at 540 °C (Fig. S2) as recently observed on YSZ [11]. However, different exchange rates are observed following the order YSZb > ZrO₂ > YSZ.

Silver is shown to greatly activate oxygen exchange, lowering the exchange temperature by as much as 230 °C in good agreement with recent results [11]. Exchange occurs through multiple heteroexchange, producing only ¹⁶O₂ during the first minutes of the experiments:

TPIE experiments performed over bare zirconia-based oxides (Fig. S1) indicated that exchange occurred through both simple and multiple heteroexchanges which correlates with similar observations reported by Zhu et al. over YSZ and ZrO₂ [33]. Weak oxygen exchange over bare SiO₂ was also reported by Martin et Duprez over 650 °C [34]. In the presence of silver, oxygen exchange is rather limited and occurs only from 450 °C.

In the presence of Ag, zirconia based samples initiate oxygen exchange at similar temperatures from 310 to 320 °C (Fig. 6). This clearly confirms that below 500 °C, the oxygen exchange only occurs on Ag NPs. Martin et Duprez reported that Rh particles size dispersed on ZrO₂, CZ and SiO₂ was also driving the exchange rate, a lower particles size leading to an increased exchange rate [34]. Oxygen exchange rates have been compared at 400 °C as, at this temperature, no ¹⁶O¹⁸O oxygen species are in the gas phase. They are quite similar when Ag NPs are dispersed on ZrO₂, YSZb and CZ and twice lower on YSZ but still in the same order of magnitude. Therefore, the nature of the support does not seem to significantly influence the surface oxygen exchange at 400 °C which is driven by Ag NPs. Rate difference between 1Ag/YSZ and 1Ag/YSZb could originate from the larger yttrium surface concentration measured over 1Ag/YSZ. We have recently shown [11] that carbonation occurs over YSZ, preferentially over Y³⁺ Lewis basic sites. Surface carbonation would lead to adsorption sites being blocked, hence limiting the oxygen exchange rate. On the other hand, amounts of exchanged bulk oxygens (¹⁶O) upon completion of the TPIE depend on the nature of the support. They are similar for both 1Ag/YSZ and 1Ag/ZrO₂. However, 1Ag/YSZb displays higher exchanged amounts of 15% instead of around 10% on 1Ag/YSZ and 1Ag/ZrO₂. This indicates that the bulk oxygen mobility is higher in YSZb than on YSZ and ZrO₂, in good agreement

Fig. 6. O_2 isotopomers molar fraction with respect to temperatures during TPIE experiments. Green line: $^{18}O_2$, red line: $^{18}O^{16}O$, blue line: $^{16}O_2$. a) 1Ag/YSZ, b) 1Ag/YSZb, c) 1Ag/ZrO₂, d) 1Ag/SiO₂, e) 1Ag/CZ. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

with the faster oxygen exchange rate observed on bare supports (Fig. S1). On 1Ag/CZ, the fraction of exchanged bulk oxygen species achieves 28.2%, most probably due to the high reducibility of CZ at 400 °C as confirmed by TPR (Fig. 5).

Soot oxidation over YSZ occurs through lattice oxygen species provided by YSZ [9]. YSZ being not reducible, we demonstrated that the limiting step of the oxidation reaction was the oxygen replenishment of YSZ lattice by the gas phase, occurring at the tpb soot/YSZ/gas in the absence of silver. This process is similar to the electrochemical reduction of oxygen in solid state electrochemical cells. Ag electrode is well-known to be one the most active for oxygen electrochemical reaction [35,36]. This explains that the replenishment was found to be greatly promoted by the presence of Ag NPs [11], as confirmed during TPIE experiments (Fig. 6).

3.3. Catalytic performances for carbon oxidation in supertight contact

3.3.1. Catalytic properties for propene cracking

Evaluation of catalytic performances toward soot oxidation is known to be highly dependent on the contact quality between soot and catalyst [37]. Loose and tight contact modes as described earlier are commonly studied, although intimate “supertight” contact was only described recently by Aneggi et al. [38]. This latter study describes a high-energy milling of CZ powder and carbon soot resulted in a thin carbon envelope containing a core of oxide. We ought to study catalysts performance for carbon oxidation under similar “supertight” contact. To obtain nanometric carbon layers covered the catalyst surface, propene cracking was performed at 600 °C over both bare supports and silver supported catalysts for 30 min. TPO was then performed to assess the amount of carbon deposited during cracking through the production of CO₂ (Table 6). No production of CO was detected. Quantity of deposited carbon is low over YSZ, YSZb and SiO₂ indicating a poor affinity of propene toward these supports. On the opposite, amounts measured over ZrO₂ and CZ are 26 and 100 times higher than over YSZ, respectively. Taking into account the SSA of the supports (Table 6), one can

distinguish three kinds of affinity between propene and support oxides: weak for YSZ and YSZb, strong for ZrO₂ and CZ and negligible for SiO₂. Carbon formation from propene cracking is dependent on the support acidity [39,40], which promotes the propene adsorption. In the case of ZrO₂, acidity originates from unsaturated Zr⁴⁺ sites at the surface [41]. Doping zirconia by silica or yttria was found to diminish the acidity [39, 42], hence explaining the lower amount of carbon deposited on YSZ and YSZb. Amount of deposited carbon with respect to the SSA was found to be 2.6 μmol/m² for YSZb against 1.3 μmol/m² for YSZ (Table 6). This correlates with the XPS data reported previously, YSZ displaying a higher Y³⁺ surface density than YSZb. Finally, amorphous SiO₂ which does not exhibit any acidic sites cannot activate propene.

Ag NPs strongly promotes the propene adsorption and cracking over non-acidic supports. Enhancement is remarkable over 1Ag/YSZ and 1Ag/YSZb as the amount of deposited carbon being increased almost tenfold. Carbon should be found on the oxide support and over the Ag NPs as the amount of deposited carbon exceeds the silver molar loading (Table 6). Smaller increase is noticeable on 1Ag/SiO₂. We suspect propene cracking only occurs in the silver particles vicinity as the molar carbon to Ag ratio is lower than 1. Concerning acidic catalysts, 1Ag/ZrO₂ and 1Ag/CZ, amounts of carbon deposited with respect to SSA are slightly lower than those obtained with bare supports. Portion of the surface might be covered by Ag NPs, hence diminishing the number of acidic sites available for propene adsorption. Therefore, propene seems to preferentially adsorb over the supports acidic sites than over Ag NPs.

3.3.2. Catalytic performances for carbon oxidation in supertight contact at iso-amount of carbon

As the amount of deposited carbon greatly differed from one catalyst to another for a propene cracking period of 30 min, we adjusted the time and the cracking temperature to obtain similar amounts over every samples (at around 40 μmoles of C). Experiments parameters and obtained carbon amounts are reported in Table 7. CZ and 1Ag/CZ affinity toward propene lead to a large amount of carbon being deposited in a short time, hence it proved to be difficult to deposit the desired quantity.

Besides, CZ specific surface properties lead to various byproducts, as parallels reactions producing large amounts of methane and CO. The latter being produced by partial oxidation of propene through the lattice oxygen stored in CZ due to the high reducibility of CZ at 600 °C. For these reason, results over CZ and 1Ag/CZ are not shown.

By adjusting the cracking time and temperature, we obtained deposited amount of carbon ranging from 29 to 43 μmol for zirconia-based supports and calcined catalysts. Experimental conditions are given in Table 6. SiO_2 and 1Ag/ SiO_2 displayed lower amounts of 1.5 and 13 μmol , respectively due to the absence of acidic sites over SiO_2 . Carbon to silver ratio indicates that the deposited carbon is located on both Ag NPs and support in the case of 1Ag/YSZ, 1Ag/YSZb and 1Ag/ ZrO_2 . On the opposite, on 1Ag/ SiO_2 , carbon deposition mainly occurs on Ag NPs. This is in good agreement with TEM micrographs displayed in Fig. 7. TEM observation was performed over calcined silver-supported samples after propene cracking (following parameters in Table 7). Over zirconia-based silver-supported catalysts, a thin carbon layer of 1–5 nm can be observed at the oxide surface and over Ag NPs. As expected from 1Ag/ SiO_2 , carbon could only be detected over Ag NPs but not on the support. In comparison with our results, carbon layer thickness obtained by Aneghi et al. through high-energy milling was about 1 nm with presence of soot clumps resulting from a too large amount of soot compared to the available catalyst surface [38].

CO_2 production observed during TPO of these samples after propene cracking are displayed in Fig. 8. Interestingly, carbon oxidation over 1Ag/ SiO_2 starts at temperature as low as 150 °C, with a maximum emission of CO_2 at 180 °C (Fig. 8d). Without Ag NPs, SiO_2 exhibits a poor activity for carbon oxidation with a negligible production of CO_2 starting at 280 °C. These results demonstrate that Ag NPs are very effective for carbon oxidation from 150 °C. However, considering low Ag loadings as in this study, the Ag/soot interface is statistically very low. For instance, the deposition of a few amount of carbon on Ag NPs was obtained only after two hours in propene at 600 °C. The temperature window of the activity, i.e. 150–250 °C, matches with that of the reduction of AgO_x species observed during TPR (Fig. 5), suggesting that metallic Ag NPs are more active than AgO_x for carbon oxidation.

Over the three other silver-supported catalysts, carbon ignition is triggered at 200 °C. In the absence of silver, carbon ignition occurs at the same temperature over YSZ and YSZb; demonstrating that in supertight contact, carbon oxidation predominantly occurs on the oxide surface, Ag NPs playing a negligible role in the soot ignition. Such effect can be explained by the wide interface existing between carbon and YSZ, leading to numerous tpb carbon/YSZ/gas which allows fast replenishment of oxygen species into the lattice. On the other hand, the carbon oxidation ignition is enhanced by Ag NPs on 1Ag/ ZrO_2 (Fig. 8c) as the ignition temperature is shifted by 40 °C. This suggests that the intrinsic activity of ZrO_2 for soot combustion is lower than that of YSZ and YSZb and confirms that Ag NPs provide active oxygen species from the gas phase as ZrO_2 is neither reducible nor ionically conductive.

On 1Ag/YSZ and 1Ag/YSZb, results show that the soot oxidation ignition is driven by the oxide support. However, the presence of Ag NPs accelerates the run-away of the reaction as the maximum of the CO_2 emissions are shifted toward lower temperatures. CO_2 maximum emission temperatures (T_{max}) is reached at 355 °C over both YSZ and YSZb. In presence of silver, T_{max} values are lowered to 325 °C and 300 °C on 1Ag/YSZ and 1Ag/YSZb, respectively. Similar behavior is observed in the case of ZrO_2 , with T_{max} values of 370 °C and 340 °C in absence and presence of silver, respectively. From these T_{max} values, one can conclude that the most efficient couple in supertight contact Ag NPs/oxide is 1Ag/YSZb.

3.4. Catalytic performances for soot oxidation of calcined catalysts in loose and tight contact modes

Silver supported catalysts performances toward soot oxidation were measured by running TPO under different conditions: loose and tight

contact modes. Only weak amounts of CO (up to 5% in total) were detected during TPO which can be attributed to silver high activity for CO oxidation [43]. Contact mode effect on soot oxidation performances is displayed in Fig. 9. We have considered two parameters: T_{10} and T_{50} , correspond to temperatures at which 10 and 50% of the soot are oxidized, respectively. T_{10} values in both contact modes range from 380 to 505 °C indicating silver-supported catalysts can be considered for DPF regeneration in term of activity. As previously reported in the literature, both T_{10} and T_{50} values are higher in loose contact mode [17,37], as soot oxidation occurs at the soot-catalyst interface, poorer contact conditions lead to lower performances. TPO experiments show the following performances order in both contact modes: 1Ag/YSZb > 1Ag/ ZrO_2 > 1Ag/YSZ > 1Ag/CZ > 1Ag/ SiO_2 .

Highest performances are obtained for 1Ag/YSZb with a T_{10} values of 380 °C in tight contact, followed by 1Ag/ ZrO_2 with 410 °C (Fig. 9). The catalyst Ag/CZ displays lower activity in both tight and loose contact modes although CZ is reported for its high activity toward soot oxidation in the literature [13,38]. As expected, the sample 1Ag/ SiO_2 is the less effective catalyst with T_{10} values of 450 and 505 °C in tight and loose contact modes, respectively.

Lower T_{50} values in the range 360–400 °C are reported in the literature for 1Ag/ ZrO_2 and 1Ag/ CeO_2 catalysts during TPO experiments [22,31]. However, TPO conditions differed from this study as soot to catalyst ratio used were 1/20 and 1/100 against 1/4 in this study. In addition, oxygen partial pressures were 10 or 20% instead of 5% in our study. Lower soot to catalyst ratio and higher oxygen partial pressure promote soot oxidation runaway as the number of soot/catalyst contact points are higher and the oxygen is more readily available, leading to lower T_{50} values.

The variations of T_{10} values as a function of the surface amount of silver, measured by XPS (Table 4) balanced by the overall silver loading (Table 1) are displayed in Fig. 10. This latter shows a linear dependence of T_{10} values with the accessible fraction of Ag NPs on the surface. Therefore, the soot ignition in both loose and tight contact modes is correlated with the fraction of Ag NPs present over the catalyst surface. Amount of surface metallic Ag NPs are related to different parameters, such as the support porosity. High pore size, as over 1Ag/CZ and 1Ag/ SiO_2 (Table 2), limits the presence of Ag NPs on the surface as they are mainly located inside pores being inaccessible to soot particles generally of the order of 100 nm size. The slope of the linear dependence is higher in loose contact mode than in tight one which indicates that the silver impact is more pronounced when the interface between soot and catalyst is limited. Propene cracking experiments proved that soot ignition occurs over YSZ oxide rather than through the Ag NPs in “supertight” contact. In the case of a more limited interface as obtained in loose contact mode, the soot oxidation is mainly activated by Ag NPs, as demonstrated in [11]. An intermediate situation occurs in tight contact mode, where both the support oxide and Ag NPs most probably participate in the soot ignition. Zirconia-based catalysts display the highest fraction of silver at their surface, while 1Ag/CZ surface concentration is intermediate and that of 1Ag/ SiO_2 is the lowest one in good agreement with soot activity measured by TPO (Fig. 9).

Fig. 10 also displays that, in spite of a similar surface concentration of Ag NPs, 1Ag/YSZb presents a lower T_{10} value in tight contact than 1Ag/YSZ, i.e. 380 °C instead of 420 °C. TPR indicates that 1Ag/YSZb contains the highest amount of metallic silver (Ag) as the amount of consumed H_2 is the lowest (Table 4). As metallic silver was reported to be the most active silver specie for soot oxidation [17,18,20,22], this could explain the 1Ag/YSZb superior activity among zirconia-based catalyst in good agreement with a higher oxygen exchange rate in the temperature domain of the soot ignition (Table 5 and Fig. 6).

3.5. Catalytic performances for soot combustion of aged catalysts in loose and tight contact modes

Hydrothermal ageing impact on catalysts catalytic activity was

Fig. 7. TEM micrographs of bare supports and silver supported catalysts after propene cracking (conditions described in Table 6): 1Ag-YSZ (a, b); 1Ag-YSZb (c, d); 1Ag-ZrO₂ (e, f); 1Ag-SiO₂ (g, h).

Fig. 8. Production of CO₂ with respect to temperature during TPO under 5%O₂/He following propene cracking (protocol described in Table 6). Bare supports: dashed curves, silver-supported catalysts: full line. (a) YSZ et Ag/YSZ, (b) YSZb et Ag/YSZb, (c) ZrO₂ et Ag/ZrO₂, (d) Ag/SiO₂ and SiO₂.

Fig. 9. T₁₀ (black) and T₅₀ (grey) obtained during TPO under 5% O₂/He in tight (full bars) and loose contact (striped bars) modes on calcined catalysts.

Table 5

Amounts of consumed ¹⁸O₂ at 400 °C and percentage of exchanged ¹⁶O₂ during TPIE experiments.

Catalysts	¹⁸ O ₂ Exchange rate at/s/g catalyst at 400 °C (x 10 ¹⁶)	% ¹⁶ O ₂ exchanged during TPIE	Oxygen exchange starting temperature (°C)
1Ag/YSZ	6.6	9.8	320
1Ag/YSZb	12	15.2	320
1Ag/ZrO ₂	14	9.7	310
1Ag/SiO ₂	—	—	450
1Ag/CZ	11	28.6	330

Fig. 10. Values of T₁₀ obtained during TPO experiments in tight (square) and loose (circle) contact under 5%O₂/He with respect to the proportion of surface silver multiplied by the amount of silver in the sample.

Table 6

Amounts of deposited carbon estimated by TPO after 30 min of propene cracking at 600 °C.

Catalysts	Deposited carbon (μmoles)	Deposited carbon with respect to SSA (μmoles/m ²)	Carbon to silver molar ratio
YSZ	3	1.3	/
YSZb	4	2.6	/
ZrO ₂	105	35.0	/
CZ	400	27.8	/
SiO ₂	2	0.01	/
1Ag-YSZ	36	14.9	1.7
1Ag-YSZb	29	24.3	1.3
1Ag-ZrO ₂	79	33.0	3.8
1Ag-CZ	367	25.5	19.8
1Ag-SiO ₂	8	0.2	0.3

Table 7

Parameters of the propene cracking: temperatures, duration and amounts of deposited carbon estimated by TPO for adjusted cracking experiments.

Catalysts	Cracking temperature (°C)	Cracking time (min)	Deposited carbon amount (μmol)	C/Ag ratio
YSZ	650	11	32	/
YSZb	650	11	36	/
ZrO ₂	580	10	33	/
SiO ₂	580	30	1.5	/
1Ag-YSZ	580	30	36	1.7
1Ag-YSZb	580	30	29	1.3
1Ag-ZrO ₂	580	10	43	2.0
1Ag-SiO ₂	580	120	13	0.4

assessed by performing TPO under 5%O₂/He in both contact conditions. T₁₀ and T₅₀ values obtained for both contact modes prior to and after ageing are reported in Tables 8 and 9. 1Ag/SiO₂ and to a less extent 1Ag/YSZ and 1Ag/ZrO₂ exhibit a remarkable hydrothermal stability as performances in tight contact mode are fairly similar after ageing (Table 8). Therefore, in spite of the observed Ag NPs loss and sintering, the Ag surface concentration remains sufficient to ignite soot combustion. 1Ag/SiO₂ stability can be explained by silver being mainly present within the pores before and after ageing without any significant Ag loss, hence displaying limited activity in both cases. On the opposite, the activity of 1Ag/YSZb significantly drops after ageing with a strong increase of T₁₀ and T₅₀ values of 60 °C and 80 °C, respectively. This could be due to the yttrium segregation on 1Ag/YSZb which was found to be strongly promoted by the ageing (Table 3), reaching the same level than that on 1Ag/YSZ. The segregation of yttrium on the surface most probably amplifies the surface carbonation by increasing the surface basicity. Surface carbonates could limit the contact points with soot and/or decorate the Ag NPs.

Catalytic performances drop are also noticeable on 1Ag/CZ with T₁₀ values increasing by 25 °C and 40 °C in tight and loose contact mode, respectively. These performances after ageing are the poorest ones in loose contact, probably due to the concomitant loss of Ag (40% wt) and sintering of the CZ support (Tables 1 and 2). Similar behavior was described by Aneggi et al. over silver-supported ceria and zirconia aged at 850 °C in presence of 10% H₂O [31]. In the case of Ag/CeO₂, T₅₀ were shifted by 40 and 50 °C in tight and loose contact, respectively. Activity loss was associated with the lower thermal stability of the support, as observed in this study.

The catalytic performances in tight contact mode are very similar for all aged catalysts except those of 1Ag/CZ (Table 8). In loose contact mode (Table 9), where the role of Ag NPs becomes predominant, 1Ag/YSZb remains the best catalyst (T₁₀ = 460 °C upon ageing), even if the activity difference with 1Ag/YSZ became small.

Table 8

Values of T₁₀ obtained during TPO under 5% O₂/He in tight contact mode for calcined and aged catalysts.

Catalysts	Tight contact mode					
	T ₁₀ calcined (°C)	T ₁₀ aged (°C)	ΔT ₁₀ (°C)	T ₅₀ calcined (°C)	T ₅₀ aged (°C)	ΔT ₅₀ (°C)
1Ag/YSZ	420	440	20	490	500	10
1Ag/YSZb	380	440	60	430	510	80
1Ag/ZrO ₂	410	435	25	470	500	30
1Ag/SiO ₂	450	450	0	490	510	20
1Ag/CZ	435	475	40	510	540	30

Table 9

Values of T₁₀ obtained during TPO under 5% O₂/He in loose contact mode for calcined and aged catalysts.

Catalysts	Loose contact mode					
	T ₁₀ calcined (°C)	T ₁₀ aged (°C)	ΔT ₁₀ (°C)	T ₅₀ calcined (°C)	T ₅₀ aged (°C)	ΔT ₅₀ (°C)
1Ag/YSZ	450	470	20	530	550	20
1Ag/YSZb	420	460	40	530	540	10
1Ag/ZrO ₂	430	485	55	550	560	10
1Ag/SiO ₂	505	505	0	580	580	0
1Ag/CZ	470	520	50	595	600	5

4. Conclusion

The impact of the soot/catalyst contact quality on the performances for soot combustion of Ag NPs dispersed on two different Ytria-Stabilised Zirconia supports (YSZ and YSZb), ZrO₂, SiO₂ and ceria-zirconia was carried out using a low Ag loading (around 1 wt%). Three contact modes were investigated: loose and tight using model soot and supertight achieved from *in-situ* deposition of nanometric layers of carbon via propene cracking. Using this latter protocol, we found that the ignition of the carbon oxidation occurs on YSZ and YSZb surface, Ag NPs only promoting the run-away of the reaction at higher temperatures. On the opposite, the Ag NPs role is significant on ZrO₂ whereas, on SiO₂, carbon is only oxidized by Ag NPs. The soot ignition in both loose and tight contact modes is clearly linked with the Ag surface concentration which was found to be high on zirconia-based catalysts, especially on YSZb, and significantly lower on ceria-zirconia. This confirms that the rate-determining step of the soot oxidation ignition on Ag/YSZ is not the YSZ active oxygen spillover but the incorporation of gaseous oxygen into YSZ. Furthermore, catalysts based on SiO₂, ZrO₂ and YSZ exhibit a remarkable hydrothermal stability as performances in tight contact mode are fairly similar after ageing.

Supporting information

Isotopic oxygen exchange on bare zirconia supports.

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