Silver-based catalytic materials for the simultaneous removal of sootand NOx

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The potential of silver-based catalysts in the simultaneous removal of particulate matter (soot) and NOxis investigated in this work and compared with that of a model Pt–Ba/Al2O3catalyst. The Ag (5 wt%) – Ba(10 wt%)/MO (MO = CeO2, ZrO2, Al2O3) and Ag (5 wt%) – Sr (10 wt%)/CeO2catalysts have been preparedby incipient wetness impregnation and characterized by BET, XRD, HRTEM, XPS and temperature-programmed reduction (TPR) experiments. The behavior of the catalyst in the soot combustion (underloose conditions) and NOxremoval has been separately analyzed by means of temperature programmedoxidation (TPO) and isothermal concentration step change (ICSC) experiments, respectively. The resultsshow that all the catalysts are active in soot combustion with a significant decrease of oxidation onsettemperature compared to uncatalyzed soot oxidation. The removal of NOxin the absence and in the pres-ence of soot was investigated under cycling conditions, i.e. alternating lean–rich phases according to theLNT strategy. It has been found that the Ag-based samples are able to simultaneously remove soot andNOx. In particular, comparing the behavior of the prepared catalysts, the Ba-containing systems showedhigher NOxstorage capacity than Sr-catalyst; also, the nitrogen selectivity increased even if resultedlower than the traditional LNT Pt-based catalyst. A detrimental effect of soot on the NOxstorage activityhas been also observed.1.

Introduction

Diesel engines are becoming very popular due to their highefficiency and low operating costs; moreover diesel engines showhigher durability than gasoline ones. However, a major envi-ronmental problem associated with diesel is the emission ofparticulate matter (PM) from the exhaust together with NOx, COand unburned hydrocarbons (HC) which has led to serious envi-ronmental problems. PM, which mostly consists of carbonaceoussoot and soluble organic fraction (SOF) of hydrocarbons that havecondensed on the soot, is a potential carcinogen, and reducing itsvolume will be an important target in the forthcoming years. Oneof the principal solution to reduce emissions from diesel exhaustsis the catalytic oxidation technique; indeed, CO and HC oxida-tion can be easily accomplished with a diesel oxidation

catalyst (DOC) [1] based on noble metals (e.g. Pt, Pd), but simultaneousreduction of NOxand soot requires complex abatement strategies[2].Among the NOxabatement technologies, the NH3/urea selectivecatalytic reduction (SCR) and the NOxstorage–reduction (NSR), alsoquoted as lean NOxtrap (LNT), are promising NOxcontrol strate-gies. On the other hand, diesel particulate filters (DPF) are usedto remove soot particles from the exhaust stream [3–6]. These fil-ters usually consist of wall-flow monoliths, that is, honeycomb-likestructures with 50% of the channels plugged at the gas entry sideand the remaining channels plugged at the exit. The gas streamenters the filter through the open channels and it is forced to passthrough the porous walls where the soot particles are trapped. DPFfilters must be regenerated by soot combustion in order to avoidpressure drop in the exhaust and several commercially availabletechnologies have been designed for this purpose [7].Catalytic oxidation of the soot is one of the most favored solu-tions proposed for the regeneration of DPF. The use of a largenumber of catalytic materials has been documented in last decade[8,9], including formulations with noble metals (mainly Pt), alkaline and alkaline earth metals or transition metals that can accomplishredox cycles (V, Mn, Co, Cu, Fe, etc.), and internal transition metals[10]. The challenges are mainly related to their low temperatureactivity and long-term thermal and chemical stability.The use of ceria (CeO2) either alone or in combination withother oxides for the oxidation of carbon particles has been reportedby several authors [11,12]. It is believed that the mechanism ofaction is based on its redox activity and its ability to deliver oxygenfrom the lattice to the carbon soot particle in a wide temperatureregion. In several studies the key role of surface area/compositionand oxygen storage capacity was taken into account and a strongrelationship between oxygen storage/redox capacity and soot com-bustion activity was found [13]. In order to enhance soot oxidationperformances of ceria, a growing number of studies have specif-ically investigated the effect of addition of silver [14–19]. Thepresence of highly reducible surface oxygen at silver–ceria inter-face was reported to positively affect the soot oxidation activityof Ag/CeO2catalysts under either oxygen or inert atmosphere [18]and the beneficial effect of silver and its ability to alter the redoxof ceria and the formation of active oxygen and peroxo species wasalso established from a theoretical point of view [17]. Aneggi et al.[15] showed that addition of Ag resulted in active soot oxidationcatalysts either on ceria and other supports like Al2O3or ZrO2; dif-ference in activity were explained by the tendency of the differentsupports in stabilizing silver in the metallic or oxide state. Forma-tion of active oxygen species on silver can be at the origin of its goodperformances even in the presence of other supports [15,18–20].Technologies for the simultaneous removal of soot and NOxarealso suggested. A possibility is to reduce NOxwith soot, while sootis being oxidized. This approach has been investigated e.g. by Kuretiet al. [21] over Fe2O3-based catalysts and by Krishna et al. [22] overCeO2-based catalysts.A different solution is the DPNR (diesel particulate NOxreduc-tion) technology that has been proposed by Toyota [23]. Thistechnology is available for both

diesel and direct-injection (DI)lean gasoline engines. The soot combustion is in this case accom-plished on the NSR (NOxstorage and reduction) catalyst duringthe NOxremoval [24,25]. NSR catalysts consist of a high surfacearea support (e.g. _-alumina), a noble metal (Pt), and an alkaline orearth-alkaline metal oxide (e.g. K, Ba, Sr) which presents a high NOxstorage capacity. The NOxremoval mechanism in the DPNR systemis that occurring on LNT catalysts [26–29]. These catalytic systemswork under cyclic conditions, alternating a lean phase during whichthe NOxproduced by the engine are adsorbed on the alkaline orearth-alkaline metal oxide component (with nitrite/nitrate speciesformation depending on the temperature [30]), and a short richphase, during which the stored nitrate species are reduced to nitro-gen. Soot abatement occurs under lean conditions thanks to the NOxstorage phase and to oxygen excess in the exhaust gas; soot removalis however claimed to occur during the rich phase as well [24].The potential utilization of a typical Pt–Ba/Al2O3NSR catalystfor the simultaneous removal of soot and NOxwas investigatedby some of us in previous works and compared with that of aPt/Al2O3sample [31–33]. It was found that the Pt–Ba/Al2O3catalystwas able to remove both soot and NOxsimultaneously, while thePt/Al2O3catalyst performed the soot oxidation effectively but wasincapable of significantly removing the gas phase NOx. Moreover,we observed that the presence of soot in the catalytic bed led to adecrease in the NOxstorage capacity (NSC) of the catalysts. How-ever, the loss of NSC measured in the presence of carbon varied asa function of the catalyst composition [10]. Soot oxidation activityand the deactivation of Al2O3-supported NSR catalysts containingPt and K were also studied [34,25,35]. The recorded results pointedout that the Pt–K/Al2O3catalyst was more active than Pt–Ba/Al2O3due to the higher mobility of the NOxspecies adsorbed on potas-sium compared to those adsorbed on barium. However, Pt–K/Al2O3catalyst showed a partial deactivation upon aging with repeatedNOxstorage–reduction cycles and soot combustion (i.e. decreasedNOxstorage capacity and also lower soot oxidation activity) [36].In this paper, we propose to combine the potential of silver-supported catalysts in the soot combustion with the NOxstoragecapacity of alkaline-earth containing catalysts. For this purpose,Ag-based catalysts supported on Al2O3, CeO2, and ZrO2have beenprepared, and doped with Ba or Sr as storage components. The sootoxidation activity has been tested at first by means of tempera-ture programmed oxidation (TPO). Then the performances of suchcatalysts in the removal of NOxand of NOx+ soot have been studied.

2. Experimental

2.1. Catalysts preparation and characterization

The Ag–Ba/MO (MO = CeO2, ZrO2, Al2O3) and Ag–Sr/CeO2cat-alysts were prepared by incipient wetness impregnation of ceria,zirconia and alumina (obtained from Grace Davison) with aque-ous solutions of silver nitrate, barium acetate and strontium nitrate(purchased from Aldrich), respectively, in order to obtain catalystswith 5 wt%

loading of Ag and 10 wt% loading of Ba or Sr. Afterimpregnation, the catalysts were dried at 100 °C overnight andcalcined under air at 500 °C for 3 h.Textural characteristics were measured according to the B.E.T.method by N_2adsorption–desorption at −196 °C, using a Tristar3000 gas adsorption analyzer (Micromeritics). Structural featuresof the catalysts were investigated by powder X-ray diffractionanalysis (XRD). Diffractograms were recorded on a Philips X'Pertdiffractometer (equipped with a real time multiple strip detector)operated at 40 kV and 40 mA with Ni-filtered Cu-K _ radiation, usinga step size of 0.02 ° and a counting time of 40 s per angular abscissain the range 20 °–80 °. The Philips X'Pert HighScore software wasused for phase identification.For high-resolution transmission electron microscopy studies(HRTEM), a JEOL JEM 2010F electron microscope equipped with afield emission gun was used working at an accelerating voltage of200 kV under bright field mode. Samples were dispersed in ethanolin an ultrasonic bath and a drop of supernatant suspension waspoured onto a holey carbon coated grid and dried completely beforemeasurements.Surface characterization was done with X-ray photoelectronspectroscopy (XPS) on a SPECS system equipped with an Al anodeXR50 source operating at 150 mW and a Phoibos 150 MCD-9 detec-tor. The pass energy of the hemispherical analyzer was set at 25 eVand the energy step was set at 0.1 eV. Charge stabilization wasachieved by using a SPECS Flood Gun FG 15/40. The sample pow-ders were pressed to self-consistent disks. Data processing wasperformed with the CasaXPS program (Casa Software Ltd., UK). Thebinding energy (BE) values were referred to the Ce 3d U___peak at916.8 eV.Temperature-programmed reduction (TPR) experiments withan AutoChem II 2920 instrument (Micromeritics) have been usedto measure the redox behavior of the catalytic materials. Samples(50–60 mg) were heated from room temperature to 800 °C at aconstant rate (10 °C/min) in a U-shaped quartz reactor, under aflowing hydrogen/argon mixture (30 ml/min, 4.6% H_2in N_2) whilemonitoring the hydrogen consumption with a TCD detector. Theoutlet gas composition was also followed by an on line quadrupolemass-spectrometer (Omnistar, Balzers Instruments).

2.2. Catalytic tests and methods

The catalytic activity for the combustion of soot was determinedfrom peak-top temperature (Tp) during temperature programmed oxidation (TPO) experiments of catalyst-soot mixtures. Printex U(Evonik-Degussa) was used as model soot, which is widely usedas a model particulate matter [37] and whose properties are welldescribed in the literature [38].A soot/catalyst weight ratio of 1:20 was used. The mixture hasbeen obtained by mixing each catalyst with soot with a spatulafor 10 min realizing a so-called loose contact [39], which indeed issimilar to the contact that arises during practical conditions. It isworth of note that the selected soot/catalyst ratio is very

commonin laboratory tests and, according to literature indications, it allowsa correct investigation of the reactivity of soot oxidation catalysts[11,40].In the TPO measurements, 20 mg of the above mixture wereheated at a constant rate ($10°C/min$) in a quartz reactor underNO/O2gas flow (10% O2(v/v) + 500 ppm NO, balance N2; totalflow 0.5 l/min). The catalyst temperature was measured by achromel–alumel thermocouple, located on the catalyst bed. Duringthe catalyst heating, no anomalous exotherms have been observed(i.e. rapid and uncontrolled increase of the temperature), suggest-ing the lack of relevant temperature gradients within the catalystbed and within the catalyst and the gas phase. As a matter offact, reproducibility of results was verified by running several TPOexperiments on similar samples and the results in terms of Tpwerealways within $±3°C$. The outlet gas composition (i.e. CO, CO2, NOand NO2) was measured by FT-IR gas analyzers (MultiGas 2030,MKS).The reactivity tests for the removal of NOxand then for thesimultaneous removal of NOxand soot were performed in a microflow-reactor apparatus consisting of a quartz tube reactor (7 mmi.d.) connected to a mass spectrometer (QMS 200, Pfeiffer Vacuum),a micro-GC (R3000, SRA) and an FT-IR analyzer (MultiGas 2030,MKS) for the on-line analysis of the outlet gases (NO, NO2, N2, H2,O2, CO, CO2, N2O and NH3). 60 mg of catalyst was used in each run.Prior the catalytic activity runs, the catalyst (without soot) has beenconditioned by performing a temperature programmed desorption(TPD) experiment followed by some storage/regeneration cyclesaccording to the ICSC procedure described below. TPD has beencarried out from room temperature up to $500°C$ ($10°C/min$) in Heand holding at this temperature 20 min. Then the temperature hasbeen decreased to $350°C$ and isothermal concentration step change(ICSC) experiments have been performed by imposing a rectangu-lar step feed of NO (1000 ppm) + 3% (v/v) O2in flowing He (leanphase). When catalyst saturation has been reached, the NO andO2concentrations have been stepwise decreased to zero, and aHe purge at the same temperature ($350°C$) has been performed.This leads to the desorption of weakly adsorbed NOxspecies. Afterthe He purge, catalyst regeneration (rich phase) has been carriedout with H2(4000 ppm) in flowing He. Conditioning lasted untila reproducible behavior was obtained; this typically required 3–4adsorption/reduction cycles. After catalyst conditioning, the DeNOxactivity of Ag–Ba/MO (MO = CeO2, ZrO2, Al2O3) and Ag–Sr/CeO2cat-alysts has been tested with typical ICSC run at $350°C$ in the absenceof soot.The DeNOx–DeSoot activity has been tested for the same cat-alysts using 66 mg of soot–catalyst loose mixture (correspondingto 59.4 mg of the bare catalyst and 6.6 mg of soot, i.e. soot load-ing (wsoot/wcat) near 11%) and performing seven storage–reductioncycles and subsequently oxidizing the residual soot by temperatureprogrammed oxidation (TPO) in 3% (v/v) O2in He from $350°C$ upto $750°C$ ($10°C/min$).Pt–Ba/Al2O3(1/20/100, w/w)

model catalyst has been also con-sidered for comparison purpose; details of catalyst preparationand characterization are reported elsewhere [41,42]. ICSC exper-iments similar to that already described have been performedover this model catalyst as also reported in previous studies[31,34].

3. Results and discussion

3.1. Structural and morphological characterization of materials

Table 1 summarizes composition and BET surface areas of thesupports and of the silver-supported catalysts. The addition of sil-ver and alkaline-earth metals results in a drop of surface area atthe loadings used in this study. This is typically observed upon addi-tion to high-surface area supports of oxides possessing high specificweight and low porosity [43,44] and the effect is more pronouncedat high loadings.The structural and morphological characteristics of the catalystswere studied by XRD, HRTEM, XPS, TG, and TPR measurements.Fig. 1 shows the X-ray diffraction profiles of barium- and strontium-doped catalysts. In the case of barium-doped materials, peaksbelonging to the supports (CeO_2, $ZrO_2$and Al_2O_3) are clearlyobserved; in addition, the presence of signals at $2\_ = 38.1°$, $44.3°$ and$64.5°$ indicates formation of metallic silver. XRD experiments revealalso the presence of orthorhombic barium carbonate whereas nocrystalline BaO is observed (with exception of Ag–Ba/Al_2O_3wherea small diffraction signal due to BaO has been detected) in agree-ment with several studies [45-47]. The weak intensities of $BaCO_3$peaks indicate a low crystallization degree of the carbonate crys-tallites on the oxides supports. Similarly, in Ag–Sr/CeO_2catalyst,signals due to metallic Ag and to $SrCO_3$are observed, in addition tothe peaks due to the support; no evidence for the presence of Ag_2Ocrystallites was obtained.HRTEM analysis of as prepared catalysts was also used with theaim to elucidate the morphology and distribution of the differentspecies present, and the results are reported in Figs. 2 and 3. Fig. 2Aand B shows representative images of the Ag–Ba/CeO_2catalyst. Thesample contains well-dispersed silver particles corresponding toFig. 1. X-ray diffraction profiles of Ag–Ba/MO (MO = CeO_2, ZrO_2, Al_2O_3) andAg–Sr/CeO_2catalysts (*CeO_2; +ZrO_2; _Al_2O_3; _$BaCO_3$; _Ag; _ $SrCO_3$).Table 1 Composition and BET surface areas of the supports and of the silver-supported catalysts. Sample SA (m^2/g) CeO_2 49 ZrO_2 59 Al_2O_3 180 Ag(5%)–Ba(10%)/CeO_2 31 Ag(5%)–Ba(10%)/ZrO_2 38 Ag(5%)–Ba(10%)/Al_2O_3 144 Ag(5%)–Sr(10%)/CeO_2 20 Fig. 2. HRTEM images of Ag–Ba/CeO_2(A and B) and Ag–Sr/CeO_2(C).both metallic Ag and Ag_2O (the latest more evident in Fig. 2B);metallic Ag nanoparticles diameter ranges about 5 nm and Ag_2Onanoparticles about 10–15 nm. The dispersion of both Ag and $Ag_2O$is good. Ag nanoparticles are identified by lattice fringes at 2.04˚Awhich correspond to the (2 0 0) crystallographic plane of metallicAg (Fig. 2A). In the FT image in Fig. 2B, the spots at 3.34 and 4.73˚Acorrespond to the (1 1 0) and (1 0 0) crystallographic planes of Ag_2O,respectively. It is worth noticing that metallic Ag is more abundantthan Ag_2O;

this is likely at the origin of the fact that X-ray diffrac-tion data reveal only the presence of metallic Ag, which might bedue to the low concentration of Ag_2O particles. Ceria crystallitesare observed, ranging about 10–20 nm in size and in close contactto both metallic Ag and Ag_2O; several ceria crystallites are identi-fied by their characteristic lattice spacing. Fig. 2C shows an imageof Ag–Sr/CeO_2sample, which is constituted by ceria crystallites ofabout 10–15 nm and a good dispersion of metallic Ag nanoparticlesof about 5 nm. This is quite similar to the Ba-containing sample;however, no Ag_2O has been detected.In Fig. 3A images of Ag–Ba/ZrO_2catalyst is reported. The samplecontains crystalline ZrO_2particles of about 20–30 nm, and in addi-tion only metallic Ag crystallites have been observed. The latticefringes at 2.04˚A at 90 ° in the FT image indicate that the Ag crys-tallite is oriented along the crystallographic direction [48]. Finally,the Ag–Ba/Al_2O_3catalyst (Fig. 3B) contains a broad distribution ofAg metal particles ranging from 5 up to 50 nm in size; accordingly,the dispersion of Ag in $Al_2O_3$is therefore poor compared to $CeO_2$and ZrO_2.The surface composition, the chemical states of the elementsand their nature were examined by the XPS technique. The bindingenergies (eV) of the most intense photoelectron Ba 3d5/2, Ag 3d5/2,Ce 3d5/2, O 1s, Zr 3p3/2, Al 2p, and Sr 3p3/2peaks of calcined catalysts,as well as atomic concentration (%) and atomic ratios are compiledin Table 2.Surface concentration of elements confirms the lowest disper-sion of the Ag–Ba/Al_2O_3sample in accordance with HRTEM. In thedeconvolution of the Ag 3d signal, fitting of the spectra can beobtained with only one doublet indicating that a single species con-stitutes most of the Ag in the samples. However, the binding energyvalues of the Ag 3d signal do not allow distinguishing between Agand Ag_2O. This is in accordance with the presence of metallic Agonly in samples containing $ZrO_2$and $Al_2O_3$and it is still compati-ble with the presence of small amount of Ag_2O with Ba containingceria-based support, in accordance with XRD results. In addition,Ag–Sr/CeO_2compared to Ag–Ba/CeO_2, shows that the amount ofSr at the surface is double than that of Ba, indicating a superiordispersion of strontium.Fig. 4(A and E) shows the temperature programmed reductionprofiles of Ag–Ba/MO (MO = CeO_2, ZrO_2, Al_2O_3) and Ag–Sr/CeO_2catalysts, respectively; inset (B) shows the TPR of the bare sup-ports. The reduction of bare ceria shows two main peaks, one atlow temperature (near 450 ° C) due to surface reduction and thesecond above 700 ° C correlated to bulk Ce^{4+}reduction [49]; theTPR profiles of the other supports (also reported in the inset (B))show a flat profile, in line with their reduction behavior underTPR conditions [50,51]. For all the catalysts, it is possible to rec-ognize two major broad regions for hydrogen consumption, one atlow temperature, centered at around 150–200 ° C, and one at hightemperature, at around 650–700 ° C. In all cases, reduction peaksat low temperature are correlated to the formation of methaneoriginating from reduction of carbonate species and likely due to anon-complete decomposition during the calcination (insets (C) and(F) show the CH_4production in the case of CeO_2-based catalysts).The higher intensity of low-temperature peak in Ag–Sr/CeO_2com-pared to Ba-doped catalysts can be associated to

the higher surfaceSr dispersion, as evidenced by XPS analysis, which might lead toa higher amount of surface carbonates. The presence of surface Baand Sr might be also responsible for the disappearance of the sur-face reduction peak of ceria. Note that in the case of ceria-supportedcatalysts a portion of the low temperature reduction peak might beassociated to reduction of surface cerium species and reduction ofsmall quantities of Ag_2O [15]. Peaks at higher temperature are associated to traces of methaneformation and desorption of carbonates and nitrites/nitrites as $CO_2$and NO respectively (insets (D) and (G) in Fig. 4); in the case ofceria, peaks at high temperature include hydrogen consumptionfor reduction of residual surface $Ce^{4+}$and bulk CeO_2[49].

3.2. Soot oxidation activity

Fig. 5A and B summarizes the results of the soot combustionexperiments (TPO) carried out in $NO/O_2/N_2$atmosphere. In Fig. 5Aare reported the two most important parameters usually usedto compare the TPO results, namely the onset temperature (graycolumn) and the peak temperature (black column). The first isevaluated in correspondence of 20 ppm of CO_2produced by theoxidation process, while the latest corresponds to the maximumproduction of CO_2.All the investigated catalysts are active in soot oxidation (Fig. 5A)with a remarkable decrease of oxidation onset temperature com-pared to uncatalyzed reaction; the catalytic oxidation is highlyselective to CO_2(only negligible amount of CO were formed),whereas the uncatalyzed reaction produces CO along with CO_2. Thehigher oxidation temperature (i.e. the lowest oxidation activity) arefound with the Al_2O_3-based catalyst, and are likely related to thelow Ag dispersion observed over these materials, while Ba and Srdo not seem to strongly influence the activity. Moreover, in all casesthe oxidation of soot is complete at the end of the experiment. Notethat the CO_2evolution profiles have regular shape with a maxi-mum near 460–470 °C and return to background level before theend of the experiment. The NO_2concentration initially increaseswith temperature due to the occurrence of the NO oxidation reac-tion; then the NO_2concentration decreases due to its involvementin the soot oxidation and to thermodynamic reasons.It is well known that metallic silver can form several sub-oxidespecies in oxidation atmosphere [52-57] and can also promote theformation of superoxide O_2^{-}ions [58]; these species might assistthe carbon oxidation by O_2[15].Also, in Fig. 5B the evolution of NO_2concentration during thesoot oxidation is reported. As it clearly appears, all the catalysts areactive in the oxidation of NO to $NO_2$and the onset temperature forthe NO_2evolution is observed below 250 °C, i.e. at a temperaturelower than the onset temperature for soot oxidation. A correlationbetween the NO_2production and the peak temperature for sootoxidation can be found. Indeed, the presence of metallic Ag caninfluence the rate of NO_2formation that in turn can be transported

Fig. 3. HRTEM images of Ag–Ba/ZrO2(A) and Ag–Ba/Al2O3(B). Fig. 4. (A) H2consumption profiles for Ag–Ba/MO (MO = CeO2, ZrO2, Al2O3) duringTPR experiment. Inset (B): H2consumption profiles for bare supports (CeO2, ZrO2,Al2O3); inset (C): production of CH4for Ag–Ba/CeO2; inset (D): evolution of CO2/NOfor Ag–Ba/CeO2. (E) H2consumption profile for Ag–Sr/CeO2catalyst. Inset (F): pro-duction of CH4for Ag–Sr/CeO2; inset (G): evolution of CO2/NO for Ag–Sr/CeO2.via the gas phase over soot particles, oxidizing carbon while beingreduced back to NO [59,60]. Therefore, both NO2-assisted and O2-promoted soot oxidation mechanisms can be observed here.

3.3. NOxand soot removal

The DeNOx(i.e. the removal of NOx) and the combinedDeNOx–DeSoot (i.e. the simultaneous removal of NOxand soot)activity has been tested at first for the CeO2-supported catalysts,namely Ag–Ba/CeO2and Ag–Sr/CeO2, in order to elucidate the roleof the storage component (i.e. of the alkaline-earth metal oxide, Bavs. Sr). Then in the case of Ba-containing catalysts the effect of thesupport (i.e. CeO2vs. ZrO2and Al2O3) has been studied as well.

3.3.1. DeNOx activity

3.3.1.1. NOx storage.

The NOxstorage/reduction activity over thefully conditioned Ag–Ba/CeO2and Ag–Sr/CeO2catalysts in theabsence of soot has been investigated at $350 \,^{\circ}C$ and the resultsreported in Fig. 6A and B, respectively. The figure shows the NO,NO2, NOx(i.e. NO + NO2) concentration profiles during the leanphase, and N2NO, NH3, H2concentration profiles measured dur-ing the rich phase; the thermal desorption in inert atmospheresubsequent to the rich phase is also reported.In the case of Ag–Ba/CeO2catalyst (Fig. 6A), NO is observed atthe reactor outlet 18 s after its admission (t = 0 s), i.e. the NO break-through is very short. Then, the NO concentration increases withtime, reaching the value of 488 ppm; at this time the NO feed isclosed. Also, NO2is immediately observed at the reactor outlet andincreases up to 454 ppm. The NO2production is related to the NOoxidation on Ag sites (NO + 1/2 O2→ NO2).Note that the NO pulse is stopped before the NOxconcentrationreached a steady level, indicating that saturation of the catalystsurface is not yet completed after 1860 s. The integral curve ofFig. 5. (A) Tonset(gray column) and Tpeak(black column) for soot combustion inNO/O2atmosphere; (B) NO2production during soot combustion in NO/O2atmo-sphere; (C) CO2production during soot combustion in NO/O2atmosphere (1,Ag–Ba/ZrO2; 2, Ag–Ba/CeO2; 3, Ag–Sr/CeO2; 4, Ag–Ba/Al2O3).stored NOxas a function of time-on-stream is plotted in Fig. 7A. TheNOxstored at this temperature at the end of adsorption are closeto 1.15×10^{-3}mol/gcat, corresponding to the involvement of 78%of the overall Ba loading by assuming the formation of Ba(NO3)2species. The exploitation of Ba sites is much higher than in the tra-ditional

Pt–Ba/Al2O3catalyst where only 20–30% of Ba participatesto the storage at $350\,^{\circ}C$ [61]; however in this case the participationof CeO2to the storage process cannot be excluded.When the NO and O2inlet concentrations are switched off(t = 1860 s and 2477 s, respectively in Fig. 6A), a tail is observedin the NOxconcentration profile, due to the desorption of weaklyadsorbed NOxspecies [62]. The net amount of stored NOxhas beencalculated by difference of the NOxadsorbed during NO feeding andthe NOxdesorbed before the regeneration phase and it is close to9.14×10^{-4}mol/gcat, corresponding to a decrease of approx. 20% ofthe initial NOxloading.In Fig. 6B the storage phase of the conditioned Ag–Sr/CeO2catalyst is reported. In this case, NO is immediately observed atthe reactor outlet upon its admission (t = 0 s), i.e. the NO break-through is zero; the NOxstored amounts up to saturation are closeto 9.45×10^{-4}mol/gcat, corresponding to 41% of the overall Sr load-ing. Notably, assuming that NOxare stored on Sr only, the amountof stored NOxis lower than that of the Ba-based sample. This couldbe explained considering the different basicity of the two alkaline

Fig. 6. Adsorption, reduction and thermal desorption phases over (A) Ag–Ba/CeO2catalyst; (B) Ag–Sr/CeO2catalyst in the absence of soot. Storage phase: 1000 ppmNO + 3% (v/v) O2in He at $350\,^{\circ}C$; reduction phase: 4000 ppm H2in He at $350\,^{\circ}C$;thermal desorption in He from $350\,^{\circ}C$ up to $500\,^{\circ}C$ ($10\,^{\circ}C/min$).Fig. 7. Integral curves of stored NOxvs. time in the absence of soot over Ag–Ba/CeO2(thick solid lines), Ag–Sr/CeO2(short dotted lines), Ag–Ba/ZrO2(dash lines) andAg–Ba/Al2O3(thin solid lines) catalysts. Integral curves of stored NOxare alsoreported for Pt–Ba/Al2O3model LNT catalyst (dashed line) for comparison purpose.earth metal components (Sr vs. Ba) which is expected to affect theNOxtrapping performances, in line with literature indications [63].Upon NO shut off, the concentrations of NO and of NO2decreasefaster than in the case of Ag–Ba/CeO2system. Also, a minor NOxdesorption has been observed closing the oxygen feed gas, resultingin a storage capacity near 7.82×10^{-4}mol/gcatat the end of thepurge.In Fig. 7 the integral curve of stored NOxvs. time for the variousinvestigated samples is shown together with that of Pt–Ba/Al2O3model LNT catalyst. The LNT model catalyst exhibits a lowerstorage capacity than that of the two CeO2-supported catalysts;in particular, the amount of stored NOxincreases in the orderPt–Ba/Al2O3< Ag–Sr/CeO2< Ag–Ba/CeO2.In Fig. 7 the integral curves of stored NOxfor Ag–Ba/ZrO2andAg–Ba/Al2O3catalysts are also reported.The CeO2-supported catalyst shows higher storage capacitythan ZrO2- and Al2O3-supported systems, being the amount ofNOxstored at steady state close to 9.14×10^{-4}mol/gcatfor theformer and near 6×10^{-4}mol/gcatvs. 7.8×10^{-4}mol/gcatfor thelatters Ag–Ba/ZrO2and Ag–Ba/Al2O3respectively. ZrO2- and Al2O3-supported catalysts instead exhibit a lower storage capacity withrespect to the traditional Pt-based LNT catalyst. From Fig. 7 it alsoappears that, after NO/O2shut off, a higher desorption of storedNOxis observed over the Ag–Ba/CeO2catalyst than over other twoBa-containing catalysts. It is worth to note that the low Ag disper-sion in Ag–Ba/Al2O3catalysts seems not to dramatically

affect theperformances of this catalyst, being comparable to Ag–Ba/ZrO2andAg–Ba/CeO2systems.3.3.1.2. Reduction of the stored NOx. The stored NOxare thenreduced under isothermal conditions by admitting H2(4000 ppm)in He and the results are shown in Fig. 6A and B for Ag–Ba/CeO2and Ag–Sr/CeO2catalysts.At 350 ◦C (Fig. 6A), upon the addition of H2(at t = 0 s), a hugeamount of NO is immediately observed at the reactor outlet alongwith lower amounts of N2and NH3. The H2consumption is notcomplete and its concentration slowly increases with time untilthe inlet value of 4000 ppm. No production of other byproductslike N2O is observed. At the end of the reduction phase (t = 7096 s inFig. 6A), a thermal desorption under inert atmosphere is carried outin order to verify the complete regeneration of the catalytic surface.Noticing, no desorption of N-containing species is observed up to500 ◦C, which indicates that the NOxstored species are all removedand that the catalytic surface is fully regenerated, as confirmed alsoby N-balance. Due to the great amounts of NO produced during thereduction, the selectivity to N2is rather low, near 37%.Similar results have been obtained in the case of Ag–Sr/CeO2catalyst (Fig. 6B); the main reduction product is NO and only smallamounts of N2and NH3are detected. The overall nitrogen selec-tivity is in this case near 22%. Moreover, during the subsequentthermal decomposition, desorption of NO is detected starting from410 ◦C; this indicates that the catalyst is not fully regenerated atthe end of the reduction phase at 350 ◦C, as confirmed also fromthe N-balance.The behavior of both Ag–Ba/CeO2and Ag–Sr/CeO2catalysts isvery different from that of Pt–Ba/Al2O3model LNT catalyst. In thelatest case, in fact, the reduction of stored species is always com-plete and the selectivity to N2is very high, near 80%, being N2themain product and NH3and NO detected in lower amounts [64].When the Ag–Ba/ZrO2and Ag–Ba/Al2O3catalysts are considered(data not shown), no substantial differences have been observedwith respect to Ag–Ba/CeO2during the reduction of stored NOx.Also in this case, the main reduction product is NO accompaniedby minor amounts of N2and NH3; accordingly, the selectivity tonitrogen is near 30%. The reduction is complete and all the storedNOxare removed at the end of this phase. It is worth to note thatthe low selectivity to N2observed in all Ag-containing catalystsshould be related to the low activity of Ag, whatever is the metaldispersion.

3.3.2. DeNOx–DeSoot activity

Lean–rich cycles have been performed also in the presence ofsoot over the Ag–Ba/CeO2and Ag–Sr/CeO2catalysts in order tostudy the simultaneous DeNOxand DeSoot activity. Fig. 8 showsa typical sequence of lean–rich phases at 350 ◦C, in terms of NO,NO2, NOx(=NO + NO2), CO2, H2, NH3and N2outlet concentrationvs. time. Fig. 8A and C refer to the first cycle over Ag–Ba/CeO2and Ag–Sr/CeO2catalysts respectively, while Fig. 8B and D refers Fig. 8. Adsorption, reduction and TPO phases over (A and B) Ag–Ba/CeO2catalyst; (C and D) Ag–Sr/CeO2catalyst in the presence of soot. (A and C): first storage–reductioncycle; (B and D): seventh storage–reduction

cycle and subsequent TPO. Storage phase: 1000 ppm NO + 3% (v/v) O_2 in He at 350 °C; reduction phase: 4000 ppm H_2 in He at 350 °C; TPO in 3% (v/v) O_2 in He from 350 °C up to 750 °C (10 °C/min).to the seventh and last cycle, followed by a TPO run up to 750 °C tocomplete the soot combustion (see Section 2).In the first lean–rich cycle over Ag–Ba/CeO_2 catalyst (Fig. 8A),upon NO and O_2 admission (at t = 0 s) the NO outlet concentra-tion increases with time after a very short NO_x breakthrough(10 s); NO_2 formation is also observed (simultaneously to NO),due to the occurrence of the oxidation of NO by O_2 at Ag sitesaccording to the stoichiometry of reaction (1). The outlet con-centrations of both NO and NO_2 increase with time, indicatingthat the NO_x storage still occurs; worth to note that the storagephase is stopped before a steady state level has been reached. Theamounts of NO_x that have been stored onto the catalyst surfaceare 2.50×10^{-5} mol/gcat, lower than that measured in the absenceof soot (9.14×10^{-4} mol/gcat, Fig. 9A), indicating a reduced storagecapacity of the catalyst in the presence of soot, as also reported inthe literature [32,33,65,66].A comparison has also been made between the NO_x stored at dif-ferent residual soot loadings, i.e. in the subsequent lean–rich cyclesduring soot oxidation, and results are shown in Fig. 9A. It appearsthat the amount of soot present in the catalyst/soot mixture influ-ences the NO_x storage behavior of the catalytic system. Accordingly,upon decreasing the residual soot loading, the NO_x storage capacityincreases, approaching that of the catalyst in the absence of soot,in line with the results over Pt–Ba/Al_2O_3 catalyst and reported bysome of us in a previous work [66]. The detrimental effect of thepresence of soot on the performances of a Pt–Ba/Al_2O_3 LNT catalystmay be related to the decrease of the NO_2 gas phase concentration,being NO_2 involved in the soot combustion, according to reaction(1): (1)As a matter of fact, the NO/NO_2 value increases from a valuenear 6 for the soot-free catalyst sample to roughly 15 in presenceof soot.In the case of Ag–Ba/CeO_2 catalyst, the NO/NO_2 ratio in theabsence and in the presence of soot changes from 1.07 to 2.1 (inthe first cycle where the higher amount of soot is present). There-fore, also in this case we can suppose the participation of NO_2 tosoot oxidation, even if the decrease in the NO_2 concentration is lessevident. Notably, oxidation by NO_2 is not likely the unique pathwayfor the soot oxidation; the direct participation of active oxygen fromceria and/or silver can also be invoked (as discussed below). Finally,note that reaction (1) may involve the intermediacy of CO althoughthis species has not been observed. In fact, CO may be oxidized toCO_2 by O_2 at Ag sites and/or by NO_2.The storage of NO_x is accompanied by the evolution of CO_2; uponNO admission, the CO_2 concentration rapidly increases (Fig. 8A)showing a maximum of 1000 ppm at the end of the storage phase.It is worth to note that its background level is not zero before NOadmission, indicating that soot oxidation occurs also in the pres-ence of O_2 alone. The presence of CO_2 in the outlet gas streamresults only from soot oxidation, being CO_2 absent the inlet feed.However, the CO_2 production is not accompanied by the evolu-tion neither of N_2 or N_2O, as reported by some authors [21,22] but$2NO_2 + C \rightarrow$

2NO + CO2 Fig. 9. Total amount of stored NOxvs. cycle number over (A) Ag–Ba/CeO2; (B)Ag–Sr/CeO2and (C) Ag–Sr/ZrO2. Filled symbols and solid lines: absence of soot;empty symbols and dashed lines: presence of soot.over different catalytic systems. The soot combustion activity of theAg–Sr/CeO2is much higher with respect to the model Pt–Ba/Al2O3,as pointed out by the higher production of CO2detected at thereactor outlet in this case (near 1000 ppm vs. near 300 ppm forPt–Ba/Al2O3[34]).It is worth noting that, upon the NO addition, the productionof CO2is much higher than that expected from the stoichiom-etry of reaction (1). This could be explained by considering thepossible "NO recycle" mechanism: in fact, similarly to the case of Pt-containing catalysts [67] it may be argued that NO which is formedin reaction (1) may be further oxidized to NO2by Ag metallic sites(recycling of NO to NO2) which could substantially enhance theefficiency of soot combustion. Moreover, as described above, sootcombustion is observed even in the absence of NO (i.e. in pres-ence of only oxygen). This suggests a direct role of the catalyst (e.g.direct participation of active oxygen from ceria and/or silver) in theoxidation of soot, which is superimposed to the soot combustionactivity by NO2. Finally, as reported in previous works [32,33,66] aspecific role of the stored NOxspecies in the soot combustion can-not be excluded, which could contribute to the significant increasein the soot combustion. These routes operate simultaneously in theoxidation of soot, so that the relevance of each pathway cannot bedetermined.Upon NO shutoff, a release of NO and NO2takes place withtime due to the desorption of the previously stored NOxspecies,and the CO2concentration decreases as well. Upon switching offthe O2feed, other NOxare also desorbed. Both desorption con-tributions appear to be remarkable if compared to those observedFig. 10. Soot conversion during the lean phase as a function of the cycle num-ber: Ag–Ba/CeO2catalyst (thick solid line); Ag–Ba/ZrO2catalyst (thin solid line);Ag–Sr/CeO2catalyst (dotted line); Pt–Ba/Al2O3catalyst (dashed line).in the soot-free catalyst, suggesting that soot has a destabilizingeffect on the NOxspecies adsorbed onto the catalytic surface; thisbehavior is in line with that observed in the case of Pt–Ba/Al2O3LNT catalyst [32,66]. The total amount of NOxdesorbed in the pres-ence and in the absence of soot are near 4.04×10^{-4} mol/gcatand2.33×10^{-4} mol/gcat, respectively; these values correspond to 94%and 20% of the NOxadsorbed species present onto the catalyticsurface at saturation. This clearly points out to a lower stability ofnitrates species in presence of soot.The reduction of the stored NOxhas also been analyzed. Reduc-tion has been carried out at the same temperature ($350 \,^\circ$C) byadmission of H2step (4000 ppm) in He. The results, reported inFig. 8A in terms of H2, NO, CO2and N2, NH3outlet concentrations asa function of time, point out that the reduction of the NOxadsorbedspecies in the presence of soot does not show significant differenceswith respect to the soot-free catalyst (compare Fig. 6A). Also in thiscase H2is immediately observed at the reactor outlet; its concen-tration increases with time, reaching the steady state level of inletconcentration. NO represents the main reduction product, alongwith minor amounts of N2and NH3. No release of other byproductslike N2O is observed; the selectivity to N2is near 45%.The data described above clearly

indicate that the Ag–Ba/CeO2catalyst is able to simultaneously store/reduce NOxand oxi-dize soot. Considering the whole sequence of the seven NOxstorage–reduction cycles (Fig. 8A and B), it appears that the behav-ior of the catalytic system is affected by the residual soot loading.Indeed, the NOxbreakthrough progressively increases during thelean/rich sequence (compare Fig. 8A with B) moving from the firstto the seventh cycle, respectively, i.e. upon increasing the soot con-version from 27% (w/w) to 85% (w/w). The increase in the deadtime is accompanied by an increase of the amount of NOxstoredduring the lean phase, from 2.50×10^{-4}mol/gcatfor the first cycleto 7.52×10^{-4}mol/gcatfor the seventh cycle (Fig. 9A), near to thatof the catalyst in the absence of soot. Note that also the NO/NO2ratio changes during soot oxidation, moving from 2.17 in the firstcycle to 0.9 in the seventh, very close to the value recorded in theabsence of soot (compare Fig. 6A with Fig. 8A and B).Fig. 10 shows the soot conversion during the lean phases asa function of the cycle number, estimated from the amounts ofevolved CO2. In the case of Ag–Ba/CeO2catalyst (solid line) duringthe lean phase of the first cycle, roughly 27% of the initial soot load-ing (6.6 mg of soot) is oxidized, which increases up to 86% during the seventh cycle. At the end of the sequence the residual soot load-ing is near 14% (w/w). In fact, the CO2concentration measured atthe end of the lean phase decreases from 980 ppm of the first cycleto 70 ppm of the seventh cycle, indicating a progressive decrease ofthe rate of soot combustion. These results are in line with the datacollected on the Pt–Ba/Al2O3LNT catalyst reported in Fig. 10 forcomparison purpose. Also in this case, the oxidation of soot takesplace progressively during the subsequent lean–rich cycles; how-ever, the oxidation ability of the Pt-based catalyst is much lowerthan that of the CeO2-based system, since in the latter case the par-ticipation of active oxygen species coming from CeO2and/or Agsites improves the oxidizing performances of the catalytic system.The behavior of Ag–Sr/CeO2catalyst in the presence of soot hasalso been tested and the results are reported in Fig. 8C (first cycle)and D (seventh cycle and TPO). The total amount of stored NOxvs.cycle number is reported in Fig. 9B, while the conversion of sootduring the lean phase as a function of the cycle number is shownin Fig. 10 (dotted line).The results clearly show that the NOxstorage capacity of theSr-containing catalyst decreases in the presence of soot; the NOxbreakthrough is still zero and the amount of stored NOxis furtherdecreased by the NOxdesorption at NO and O2shut off, so at theend of the first storage phase 1.15×10^{-4}mol/gcatare present atcatalyst surface (vs. 7.82×10^{-4}mol/gcat). Moreover, the NO/NO2ratio changes from 3.88 in the first cycle to 2.65 in the seventh one,and it does not reach the initial value of 1.58 in the absence of soot.The detrimental effect of soot on the storage capacity of Ag–Sr/CeO2catalyst seems to be independent from the amount of residual soot,i.e. at the end of the seventh cycle the catalyst does not recoverits original performance, when more than 60% of soot has beenoxidized (see Fig. 10). Also the soot oxidation capability is lowerthan in case of Ag–Ba/CeO2catalyst; indeed, a soot conversion

of13% is observed in the first cycle increasing up to 74% in the seventhone. Accordingly, the combustion of soot is completed during thesubsequent final TPO run.Finally, the effect of soot on the storage capacity has been stud-ied also in the case of Ag–Ba/ZrO2catalyst and the results in termsof stored NOxvs. cycle number are reported in Fig. 9C. The behavioris qualitatively similar to that observed in the case of CeO2-basedcatalysts; indeed, the amount of stored NOxdecreases in the pres-ence of soot and the system partially recover the storage capacityexhibited in the absence of soot only when most of the soot presentis burnt. On the other hand, the soot conversion reported in Fig. 10is lower than that of Ag–Ba/CeO2at the beginning and increases upto 90% at the end of the lean–rich sequence.4. ConclusionsThe study focuses on the catalytic behavior of Ag-based cata-lysts in both soot oxidation and simultaneous removal of soot andNOx. The results have been compared with that obtained on thereference Pt–Ba/Al2O3LNT catalyst.It has been found that all the Ag-containing catalysts are able tooxidize soot in the presence of NO/O2at temperatures near 250 ◦C,remarkably lower than the uncatalyzed soot oxidation; the pres-ence of Ba or Sr does not significantly affect the catalytic activity.On the other hand, the Ag dispersion improves the oxidation activ-ity, i.e. the catalyst with lower Ag dispersion exhibits higher onsetoxidation temperature.All the Ag-containing catalysts are able to simultaneouslyremove soot and NOx, when operating under isothermal cyclingconditions, i.e. alternating lean–rich phases according to the typ-ical DPNR strategy. The data show that in the absence of soot thestorage capacity of the investigated systems is higher than that oftraditional Pt–Ba/Al2O3LNT catalyst; however, in the presence ofsoot, the detrimental effect of soot on the storage capacity is moreevident in the case of Ag-based catalysts. The latters are by far moreactive in the soot combustion than the Pt-based catalyst, possiblydue to the participation of oxygen active species from ceria and/orsilver.In conclusion, the results point out that Ag-based catalystsshould be considered as a promising alternative to Pt-based cat-alysts for the simultaneous removal of soot and NOx. However,their reactivity in the reduction of the stored NOxshould be furtherenhanced to improve the N2selectivity.

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