

Silver-based catalytic materials for the simultaneous removal of soot and NO_x

Lidia Castoldi^{a,*}, Eleonora Aneggi^b, Roberto Matarrese^a, Rossella Bonzia, Jordi Llorca^c,
Alessandro Trovarelli^{b,*}, Luca Lietti^a

^aPolitecnico di Milano, Dipartimento di Energia, via La Masa 34, 20156 Milano, Italy

^bUniversità di Udine, DCFA, via Cottonificio 108, 33100 Udine, Italy

^cInstitute of Energy Technologies and Centre for Research in NanoEngineering, Universitat Politècnica de Catalunya, Diagonal 647, 08028 Barcelona, Spain

The potential of silver-based catalysts in the simultaneous removal of particulate matter (soot) and NO_x is investigated in this work and compared with that of a model Pt–Ba/Al₂O₃ catalyst. The Ag (5 wt%) – Ba(10 wt%)/MO (MO = CeO₂, ZrO₂, Al₂O₃) and Ag (5 wt%) – Sr (10 wt%)/CeO₂ catalysts have been prepared by 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 (under loose conditions) and NO_x removal has been separately analyzed by means of temperature programmed oxidation (TPO) and isothermal concentration step change (ICSC) experiments, respectively. The results show that all the catalysts are active in soot combustion with a significant decrease of oxidation onset temperature compared to uncatalyzed soot oxidation. The removal of NO_x in the absence and in the presence of soot was investigated under cycling conditions, i.e. alternating lean–rich phases according to the LNT strategy. It has been found that the Ag-based samples are able to simultaneously remove soot and NO_x. In particular, comparing the behavior of the prepared catalysts, the Ba-containing systems showed higher NO_x storage capacity than Sr-catalyst; also, the nitrogen selectivity increased even if resulted lower than the traditional LNT Pt-based catalyst. A detrimental effect of soot on the NO_x storage activity has been also observed. 1.

Introduction

Diesel engines are becoming very popular due to their high efficiency and low operating costs; moreover diesel engines show higher durability than gasoline ones. However, a major environmental problem associated with diesel is the emission of particulate matter (PM) from the exhaust together with NO_x, CO and unburned hydrocarbons (HC) which has led to serious environmental problems. PM, which mostly consists of carbonaceous soot and soluble organic fraction (SOF) of hydrocarbons that have condensed on the soot, is a potential carcinogen, and reducing its volume will be an important target in the forthcoming years. One of the principal solutions to reduce emissions from diesel exhaust is the catalytic oxidation technique; indeed, CO and HC oxidation can be easily accomplished with a diesel oxidation

catalyst (DOC) [1] based on noble metals (e.g. Pt, Pd), but simultaneous reduction of NO_x and soot requires complex abatement strategies [2]. Among the NO_x abatement technologies, the NH₃/urea selective catalytic reduction (SCR) and the NO_x storage–reduction (NSR), also quoted as lean NO_x trap (LNT), are promising NO_x control strategies. On the other hand, diesel particulate filters (DPF) are used to remove soot particles from the exhaust stream [3–6]. These filters usually consist of wall-flow monoliths, that is, honeycomb-like structures with 50% of the channels plugged at the gas entry side and the remaining channels plugged at the exit. The gas stream enters the filter through the open channels and it is forced to pass through the porous walls where the soot particles are trapped. DPF filters must be regenerated by soot combustion in order to avoid pressure drop in the exhaust and several commercially available technologies have been designed for this purpose [7]. Catalytic oxidation of the soot is one of the most favored solutions proposed for the regeneration of DPF. The use of a large number 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 accomplish redox cycles (V, Mn, Co, Cu, Fe, etc.), and internal transition metals [10]. The challenges are mainly related to their low temperature activity and long-term thermal and chemical stability. The use of ceria (CeO₂) either alone or in combination with other oxides for the oxidation of carbon particles has been reported by several authors [11,12]. It is believed that the mechanism of action is based on its redox activity and its ability to deliver oxygen from the lattice to the carbon soot particle in a wide temperature region. In several studies the key role of surface area/composition and oxygen storage capacity was taken into account and a strong relationship between oxygen storage/redox capacity and soot combustion activity was found [13]. In order to enhance soot oxidation performances of ceria, a growing number of studies have specifically investigated the effect of addition of silver [14–19]. The presence of highly reducible surface oxygen at silver–ceria interface was reported to positively affect the soot oxidation activity of Ag/CeO₂ catalysts under either oxygen or inert atmosphere [18] and the beneficial effect of silver and its ability to alter the redox of ceria and the formation of active oxygen and peroxy species was also established from a theoretical point of view [17]. Aneggi et al. [15] showed that addition of Ag resulted in active soot oxidation catalysts either on ceria and other supports like Al₂O₃ or ZrO₂; difference in activity were explained by the tendency of the different supports in stabilizing silver in the metallic or oxide state. Formation of active oxygen species on silver can be at the origin of its good performances even in the presence of other supports [15,18–20]. Technologies for the simultaneous removal of soot and NO_x are also suggested. A possibility is to reduce NO_x with soot, while soot is being oxidized. This approach has been investigated e.g. by Kuret et al. [21] over Fe₂O₃-based catalysts and by Krishna et al. [22] over CeO₂-based catalysts. A different solution is the DPNR (diesel particulate NO_x reduction) technology that has been proposed by Toyota [23]. This technology is available for both

diesel and direct-injection (DI) lean gasoline engines. The soot combustion is in this case accomplished on the NSR (NO_x storage and reduction) catalyst during the NO_x removal [24,25]. NSR catalysts consist of a high surface area support (e.g. γ -alumina), a noble metal (Pt), and an alkaline or earth-alkaline metal oxide (e.g. K, Ba, Sr) which presents a high NO_x storage capacity. The NO_x removal mechanism in the DPNR system is that occurring on LNT catalysts [26–29]. These catalytic systems work under cyclic conditions, alternating a lean phase during which the NO_x produced by the engine are adsorbed on the alkaline or earth-alkaline metal oxide component (with nitrite/nitrate species formation depending on the temperature [30]), and a short rich phase, during which the stored nitrate species are reduced to nitrogen. Soot abatement occurs under lean conditions thanks to the NO_x storage phase and to oxygen excess in the exhaust gas; soot removal is however claimed to occur during the rich phase as well [24]. The potential utilization of a typical Pt–Ba/Al₂O₃ NSR catalyst for the simultaneous removal of soot and NO_x was investigated by some of us in previous works and compared with that of a Pt/Al₂O₃ sample [31–33]. It was found that the Pt–Ba/Al₂O₃ catalyst was able to remove both soot and NO_x simultaneously, while the Pt/Al₂O₃ catalyst performed the soot oxidation effectively but was incapable of significantly removing the gas phase NO_x. Moreover, we observed that the presence of soot in the catalytic bed led to a decrease in the NO_x storage capacity (NSC) of the catalysts. However, the loss of NSC measured in the presence of carbon varied as a function of the catalyst composition [10]. Soot oxidation activity and the deactivation of Al₂O₃-supported NSR catalysts containing Pt and K were also studied [34,25,35]. The recorded results pointed out that the Pt–K/Al₂O₃ catalyst was more active than Pt–Ba/Al₂O₃ due to the higher mobility of the NO_x species adsorbed on potassium compared to those adsorbed on barium. However, Pt–K/Al₂O₃ catalyst showed a partial deactivation upon aging with repeated NO_x storage–reduction cycles and soot combustion (i.e. decreased NO_x storage 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 NO_x storage capacity of alkaline-earth containing catalysts. For this purpose, Ag-based catalysts supported on Al₂O₃, CeO₂, and ZrO₂ have been prepared, and doped with Ba or Sr as storage components. The soot oxidation activity has been tested at first by means of temperature programmed oxidation (TPO). Then the performances of such catalysts in the removal of NO_x and of NO_x+ soot have been studied.

2. Experimental

2.1. Catalysts preparation and characterization

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

loading of Ag and 10 wt% loading of Ba or Sr. After impregnation, the catalysts were dried at 100 °C overnight and calcined under air at 500 °C for 3 h. Textural characteristics were measured according to the B.E.T. method by N₂ adsorption–desorption at –196 °C, using a Tristar3000 gas adsorption analyzer (Micromeritics). Structural features of the catalysts were investigated by powder X-ray diffraction analysis (XRD). Diffractograms were recorded on a Philips X'Pert diffractometer (equipped with a real time multiple strip detector) operated at 40 kV and 40 mA with Ni-filtered Cu-K_α radiation, using a step size of 0.02 ° and a counting time of 40 s per angular abscissa in the range 20 °–80 °. The Philips X'Pert HighScore software was used for phase identification. For high-resolution transmission electron microscopy studies (HRTEM), a JEOL JEM 2010F electron microscope equipped with a field emission gun was used working at an accelerating voltage of 200 kV under bright field mode. Samples were dispersed in ethanol in an ultrasonic bath and a drop of supernatant suspension was poured onto a holey carbon coated grid and dried completely before measurements. Surface characterization was done with X-ray photoelectron spectroscopy (XPS) on a SPECS system equipped with an Al anode XR50 source operating at 150 mW and a Phoibos 150 MCD-9 detector. The pass energy of the hemispherical analyzer was set at 25 eV and the energy step was set at 0.1 eV. Charge stabilization was achieved by using a SPECS Flood Gun FG 15/40. The sample powders were pressed to self-consistent disks. Data processing was performed with the CasaXPS program (Casa Software Ltd., UK). The binding energy (BE) values were referred to the Ce 3d U₃ peak at 916.8 eV. Temperature-programmed reduction (TPR) experiments with an AutoChem II 2920 instrument (Micromeritics) have been used to measure the redox behavior of the catalytic materials. Samples (50–60 mg) were heated from room temperature to 800 °C at a constant rate (10 °C/min) in a U-shaped quartz reactor, under a flowing hydrogen/argon mixture (30 ml/min, 4.6% H₂ in N₂) while monitoring the hydrogen consumption with a TCD detector. The outlet gas composition was also followed by an on line quadrupole mass-spectrometer (Omnistar, Balzers Instruments).

2.2. Catalytic tests and methods

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

common in laboratory tests and, according to literature indications, it allows a correct investigation of the reactivity of soot oxidation catalysts [11,40]. In the TPO measurements, 20 mg of the above mixture were heated at a constant rate ($10^{\circ}\text{C}/\text{min}$) in a quartz reactor under NO/O_2 gas flow ($10\% \text{O}_2(\text{v}/\text{v}) + 500 \text{ ppm NO}$, balance N_2 ; total flow $0.5 \text{ l}/\text{min}$). The catalyst temperature was measured by a chromel–alumel thermocouple, located on the catalyst bed. During the catalyst heating, no anomalous exotherms have been observed (i.e. rapid and uncontrolled increase of the temperature), suggesting the lack of relevant temperature gradients within the catalyst bed and within the catalyst and the gas phase. As a matter of fact, reproducibility of results was verified by running several TPO experiments on similar samples and the results in terms of T_p were always within $\pm 3^{\circ}\text{C}$. The outlet gas composition (i.e. CO , CO_2 , NO and NO_2) was measured by FT-IR gas analyzers (MultiGas 2030, MKS). The reactivity tests for the removal of NO_x and then for the simultaneous removal of NO_x and soot were performed in a microflow-reactor apparatus consisting of a quartz tube reactor (7 mm i.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 , NO_2 , N_2 , H_2 , O_2 , CO , CO_2 , N_2O and NH_3). 60 mg of catalyst was used in each run. Prior the catalytic activity runs, the catalyst (without soot) has been conditioned by performing a temperature programmed desorption (TPD) experiment followed by some storage/regeneration cycles according to the ICSC procedure described below. TPD has been carried out from room temperature up to 500°C ($10^{\circ}\text{C}/\text{min}$) in He and holding at this temperature 20 min. Then the temperature has been decreased to 350°C and isothermal concentration step change (ICSC) experiments have been performed by imposing a rectangular step feed of NO (1000 ppm) + $3\% (\text{v}/\text{v}) \text{O}_2$ in flowing He (lean phase). When catalyst saturation has been reached, the NO and O_2 concentrations have been stepwise decreased to zero, and a He purge at the same temperature (350°C) has been performed. This leads to the desorption of weakly adsorbed NO_x species. After the He purge, catalyst regeneration (rich phase) has been carried out with H_2 (4000 ppm) in flowing He. Conditioning lasted until a reproducible behavior was obtained; this typically required 3–4 adsorption/reduction cycles. After catalyst conditioning, the De NO_x activity of Ag–Ba/MO (MO = CeO_2 , ZrO_2 , Al_2O_3) and Ag–Sr/ CeO_2 catalysts has been tested with typical ICSC run at 350°C in the absence of soot. The De NO_x –DeSoot activity has been tested for the same catalysts using 66 mg of soot–catalyst loose mixture (corresponding to 59.4 mg of the bare catalyst and 6.6 mg of soot, i.e. soot loading ($w_{\text{soot}}/w_{\text{cat}}$) near 11%) and performing seven storage–reduction cycles and subsequently oxidizing the residual soot by temperature programmed oxidation (TPO) in $3\% (\text{v}/\text{v}) \text{O}_2$ in He from 350°C up to 750°C ($10^{\circ}\text{C}/\text{min}$). Pt–Ba/ Al_2O_3 (1/20/100, w/w)

model catalyst has been also considered for comparison purpose; details of catalyst preparation and characterization are reported elsewhere [41,42]. ICSC experiments similar to that already described have been performed over 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 the supports and of the silver-supported catalysts. The addition of silver and alkaline-earth metals results in a drop of surface area at the loadings used in this study. This is typically observed upon addition to high-surface area supports of oxides possessing high specific weight and low porosity [43,44] and the effect is more pronounced at high loadings. The structural and morphological characteristics of the catalysts were 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, peaks belonging to the supports (CeO₂, ZrO₂ and Al₂O₃) are clearly observed; in addition, the presence of signals at $2\theta = 38.1^\circ$, 44.3° and 64.5° indicates formation of metallic silver. XRD experiments reveal also the presence of orthorhombic barium carbonate whereas no crystalline BaO is observed (with exception of Ag–Ba/Al₂O₃ where a small diffraction signal due to BaO has been detected) in agreement with several studies [45–47]. The weak intensities of BaCO₃ peaks indicate a low crystallization degree of the carbonate crystallites on the oxides supports. Similarly, in Ag–Sr/CeO₂ catalyst, signals due to metallic Ag and to SrCO₃ are observed, in addition to the peaks due to the support; no evidence for the presence of Ag₂O crystallites was obtained. HRTEM analysis of as prepared catalysts was also used with the aim to elucidate the morphology and distribution of the different species present, and the results are reported in **Figs. 2 and 3**. **Fig. 2A** and **B** shows representative images of the Ag–Ba/CeO₂ catalyst. This sample contains well-dispersed silver particles corresponding to **Fig. 1**. X-ray diffraction profiles of Ag–Ba/MO (MO = CeO₂, ZrO₂, Al₂O₃) and Ag–Sr/CeO₂ catalysts (*CeO₂; +ZrO₂; _Al₂O₃; _BaCO₃; _Ag; _SrCO₃). **Table 1** Composition and BET surface areas of the supports and of the silver-supported catalysts. Sample SA (m²/g) CeO₂ 49 ZrO₂ 59 Al₂O₃ 180 Ag(5%)–Ba(10%)/CeO₂ 31 Ag(5%)–Ba(10%)/ZrO₂ 38 Ag(5%)–Ba(10%)/Al₂O₃ 144 Ag(5%)–Sr(10%)/CeO₂ 20 **Fig. 2**. HRTEM images of Ag–Ba/CeO₂ (A and B) and Ag–Sr/CeO₂ (C). both metallic Ag and Ag₂O (the latest more evident in **Fig. 2B**); metallic Ag nanoparticles diameter ranges about 5 nm and Ag₂O nanoparticles about 10–15 nm. The dispersion of both Ag and Ag₂O is good. Ag nanoparticles are identified by lattice fringes at 2.04° which correspond to the (2 0 0) crystallographic plane of metallic Ag (**Fig. 2A**). In the FT image in **Fig. 2B**, the spots at 3.34° and 4.73° correspond to the (1 1 0) and (1 0 0) crystallographic planes of Ag₂O, respectively. It is worth noticing that metallic Ag is more abundant than Ag₂O;

this is likely at the origin of the fact that X-ray diffraction data reveal only the presence of metallic Ag, which might be due to the low concentration of Ag₂O particles. Ceria crystallites are observed, ranging about 10–20 nm in size and in close contact to both metallic Ag and Ag₂O; several ceria crystallites are identified by their characteristic lattice spacing. Fig. 2C shows an image of Ag–Sr/CeO₂ sample, which is constituted by ceria crystallites of about 10–15 nm and a good dispersion of metallic Ag nanoparticles of about 5 nm. This is quite similar to the Ba-containing sample; however, no Ag₂O has been detected. In Fig. 3A images of Ag–Ba/ZrO₂ catalyst is reported. The sample contains crystalline ZrO₂ particles of about 20–30 nm, and in addition only metallic Ag crystallites have been observed. The lattice fringes at 2.04 Å at 90° in the FT image indicate that the Ag crystallite is oriented along the crystallographic direction [48]. Finally, the Ag–Ba/Al₂O₃ catalyst (Fig. 3B) contains a broad distribution of Ag metal particles ranging from 5 up to 50 nm in size; accordingly, the dispersion of Ag in Al₂O₃ is therefore poor compared to CeO₂ and ZrO₂. The surface composition, the chemical states of the elements and their nature were examined by the XPS technique. The binding energies (eV) of the most intense photoelectron Ba 3d_{5/2}, Ag 3d_{5/2}, Ce 3d_{5/2}, O 1s, Zr 3p_{3/2}, Al 2p, and Sr 3p_{3/2} peaks of calcined catalysts, as well as atomic concentration (%) and atomic ratios are compiled in Table 2. Surface concentration of elements confirms the lowest dispersion of the Ag–Ba/Al₂O₃ sample in accordance with HRTEM. In the deconvolution of the Ag 3d signal, fitting of the spectra can be obtained with only one doublet indicating that a single species constitutes most of the Ag in the samples. However, the binding energy values of the Ag 3d signal do not allow distinguishing between Ag and Ag₂O. This is in accordance with the presence of metallic Ag only in samples containing ZrO₂ and Al₂O₃ and it is still compatible with the presence of small amount of Ag₂O with Ba containing ceria-based support, in accordance with XRD results. In addition, Ag–Sr/CeO₂ compared to Ag–Ba/CeO₂, shows that the amount of Sr at the surface is double than that of Ba, indicating a superior dispersion of strontium. Fig. 4(A and E) shows the temperature programmed reduction profiles of Ag–Ba/MO (MO = CeO₂, ZrO₂, Al₂O₃) and Ag–Sr/CeO₂ catalysts, respectively; inset (B) shows the TPR of the bare supports. The reduction of bare ceria shows two main peaks, one at low temperature (near 450 °C) due to surface reduction and the second above 700 °C correlated to bulk Ce⁴⁺ reduction [49]; the TPR profiles of the other supports (also reported in the inset (B)) show a flat profile, in line with their reduction behavior under TPR conditions [50,51]. For all the catalysts, it is possible to recognize two major broad regions for hydrogen consumption, one at low temperature, centered at around 150–200 °C, and one at high temperature, at around 650–700 °C. In all cases, reduction peaks at low temperature are correlated to the formation of methane originating from reduction of carbonate species and likely due to an incomplete decomposition during the calcination (insets (C) and (F) show the CH₄ production in the case of CeO₂-based catalysts). The higher intensity of low-temperature peak in Ag–Sr/CeO₂ compared to Ba-doped catalysts can be associated to

the higher surface Sr dispersion, as evidenced by XPS analysis, which might lead to a higher amount of surface carbonates. The presence of surface Ba and Sr might be also responsible for the disappearance of the surface reduction peak of ceria. Note that in the case of ceria-supported catalysts a portion of the low temperature reduction peak might be associated to reduction of surface cerium species and reduction of small quantities of Ag₂O [15]. Peaks at higher temperature are associated to traces of methane formation and desorption of carbonates and nitrates/nitrites as CO₂ and NO respectively (insets (D) and (G) in Fig. 4); in the case of ceria, peaks at high temperature include hydrogen consumption for reduction of residual surface Ce⁴⁺ and bulk CeO₂ [49].

3.2. Soot oxidation activity

Fig. 5A and B summarizes the results of the soot combustion experiments (TPO) carried out in NO/O₂/N₂ atmosphere. In Fig. 5A are reported the two most important parameters usually used to compare the TPO results, namely the onset temperature (gray column) and the peak temperature (black column). The first is evaluated in correspondence of 20 ppm of CO₂ produced by the oxidation process, while the latest corresponds to the maximum production of CO₂. All the investigated catalysts are active in soot oxidation (Fig. 5A) with a remarkable decrease of oxidation onset temperature compared to uncatalyzed reaction; the catalytic oxidation is highly selective to CO₂ (only negligible amount of CO were formed), whereas the uncatalyzed reaction produces CO along with CO₂. The higher oxidation temperature (i.e. the lowest oxidation activity) are found with the Al₂O₃-based catalyst, and are likely related to the low Ag dispersion observed over these materials, while Ba and Sr do not seem to strongly influence the activity. Moreover, in all cases the oxidation of soot is complete at the end of the experiment. Note that the CO₂ evolution profiles have regular shape with a maximum near 460–470 °C and return to background level before the end of the experiment. The NO₂ concentration initially increases with temperature due to the occurrence of the NO oxidation reaction; then the NO₂ concentration decreases due to its involvement in the soot oxidation and to thermodynamic reasons. It is well known that metallic silver can form several suboxide species in oxidation atmosphere [52-57] and can also promote the formation of superoxide O₂⁻ ions [58]; these species might assist the carbon oxidation by O₂ [15]. Also, in Fig. 5B the evolution of NO₂ concentration during the soot oxidation is reported. As it clearly appears, all the catalysts are active in the oxidation of NO to NO₂ and the onset temperature for the NO₂ evolution is observed below 250 °C, i.e. at a temperature lower than the onset temperature for soot oxidation. A correlation between the NO₂ production and the peak temperature for soot oxidation can be found. Indeed, the presence of metallic Ag can influence the rate of NO₂ formation 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. NO_xand soot removal

The DeNO_x(i.e. the removal of NO_x) and the combinedDeNO_x–DeSoot (i.e. the simultaneous removal of NO_xand 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. DeNO_x activity

3.3.1.1. NO_x storage.

The NO_xstorage/reduction activity over thefully conditioned Ag–Ba/CeO₂and Ag–Sr/CeO₂catalysts in theabsence of soot has been investigated at 350 °C and the resultsreported in Fig. 6A and B, respectively. The figure shows the NO,NO₂, NO_x(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 NO_xconcentrationreached a steady level, indicating that saturation of the catalystsurface is not yet completed after 1860 s. The integral curve ofFig. 5. (A) T_{onset}(gray column) and T_{peak}(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 NO_xas a function of time-on-stream is plotted in Fig. 7A. TheNO_xstored 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/Al₂O₃ catalyst where only 20–30% of Ba participate to the storage at 350 °C [61]; however in this case the participation of CeO₂ to the storage process cannot be excluded. When the NO and O₂ inlet concentrations are switched off (t = 1860 s and 2477 s, respectively in Fig. 6A), a tail is observed in the NO_x concentration profile, due to the desorption of weakly adsorbed NO_x species [62]. The net amount of stored NO_x has been calculated by difference of the NO_x adsorbed during NO feeding and the NO_x desorbed before the regeneration phase and it is close to 9.14×10^{-4} mol/gcat, corresponding to a decrease of approx. 20% of the initial NO_x loading. In Fig. 6B the storage phase of the conditioned Ag–Sr/CeO₂ catalyst is reported. In this case, NO is immediately observed at the reactor outlet upon its admission (t = 0 s), i.e. the NO break-through is zero; the NO_x stored amounts up to saturation are close to 9.45×10^{-4} mol/gcat, corresponding to 41% of the overall Sr loading. Notably, assuming that NO_x are stored on Sr only, the amount of stored NO_x is lower than that of the Ba-based sample. This could be explained considering the different basicity of the two alkaline earth metal components (Sr vs. Ba) which is expected to affect the NO_x trapping performances, in line with literature indications [63]. Upon NO shut off, the concentrations of NO and of NO₂ decrease faster than in the case of Ag–Ba/CeO₂ system. Also, a minor NO_x desorption has been observed closing the oxygen feed gas, resulting in a storage capacity near 7.82×10^{-4} mol/gcat at the end of the purge. In Fig. 7 the integral curve of stored NO_x vs. time for the various investigated samples is shown together with that of Pt–Ba/Al₂O₃ model LNT catalyst. The LNT model catalyst exhibits a lower storage capacity than that of the two CeO₂-supported catalysts; in particular, the amount of stored NO_x increases in the order Pt–Ba/Al₂O₃ < Ag–Sr/CeO₂ < Ag–Ba/CeO₂. In Fig. 7 the integral curves of stored NO_x for Ag–Ba/ZrO₂ and Ag–Ba/Al₂O₃ catalysts are also reported. The CeO₂-supported catalyst shows higher storage capacity than ZrO₂- and Al₂O₃-supported systems, being the amount of NO_x stored at steady state close to 9.14×10^{-4} mol/gcat for the former and near 6×10^{-4} mol/gcat vs. 7.8×10^{-4} mol/gcat for the latter Ag–Ba/ZrO₂ and Ag–Ba/Al₂O₃ respectively. ZrO₂- and Al₂O₃-supported catalysts instead exhibit a lower storage capacity with respect to the traditional Pt-based LNT catalyst. From Fig. 7 it also appears that, after NO/O₂ shut off, a higher desorption of stored NO_x is observed over the Ag–Ba/CeO₂ catalyst than over other two Ba-containing catalysts. It is worth to note that the low Ag dispersion in Ag–Ba/Al₂O₃ catalysts seems not to dramatically

affect the performances of this catalyst, being comparable to Ag–Ba/ZrO₂ and Ag–Ba/CeO₂ systems.

3.3.1.2. Reduction of the stored NO_x.

The stored NO_x are then reduced under isothermal conditions by admitting H₂ (4000 ppm) in He and the results are shown in Fig. 6A and B for Ag–Ba/CeO₂ and Ag–Sr/CeO₂ catalysts. At 350 °C (Fig. 6A), upon the addition of H₂ (at $t = 0$ s), a huge amount of NO is immediately observed at the reactor outlet along with lower amounts of N₂ and NH₃. The H₂ consumption is not complete and its concentration slowly increases with time until the inlet value of 4000 ppm. No production of other byproducts like N₂O is observed. At the end of the reduction phase ($t = 7096$ s in Fig. 6A), a thermal desorption under inert atmosphere is carried out in order to verify the complete regeneration of the catalytic surface. Noticing, no desorption of N-containing species is observed up to 500 °C, which indicates that the NO_x stored species are all removed and that the catalytic surface is fully regenerated, as confirmed also by N-balance. Due to the great amounts of NO produced during the reduction, the selectivity to N₂ is rather low, near 37%. Similar results have been obtained in the case of Ag–Sr/CeO₂ catalyst (Fig. 6B); the main reduction product is NO and only small amounts of N₂ and NH₃ are detected. The overall nitrogen selectivity is in this case near 22%. Moreover, during the subsequent thermal decomposition, desorption of NO is detected starting from 410 °C; this indicates that the catalyst is not fully regenerated at the end of the reduction phase at 350 °C, as confirmed also from the N-balance. The behavior of both Ag–Ba/CeO₂ and Ag–Sr/CeO₂ catalysts is very different from that of Pt–Ba/Al₂O₃ model LNT catalyst. In the latest case, in fact, the reduction of stored species is always complete and the selectivity to N₂ is very high, near 80%, being N₂ the main product and NH₃ and NO detected in lower amounts [64]. When the Ag–Ba/ZrO₂ and Ag–Ba/Al₂O₃ catalysts are considered (data not shown), no substantial differences have been observed with respect to Ag–Ba/CeO₂ during the reduction of stored NO_x. Also in this case, the main reduction product is NO accompanied by minor amounts of N₂ and NH₃; accordingly, the selectivity to nitrogen is near 30%. The reduction is complete and all the stored NO_x are removed at the end of this phase. It is worth to note that the low selectivity to N₂ observed in all Ag-containing catalysts should be related to the low activity of Ag, whatever is the metal dispersion.

3.3.2. DeNO_x–DeSoot activity

Lean–rich cycles have been performed also in the presence of soot over the Ag–Ba/CeO₂ and Ag–Sr/CeO₂ catalysts in order to study the simultaneous DeNO_x and DeSoot activity. Fig. 8 shows a typical sequence of lean–rich phases at 350 °C, in terms of NO, NO₂, NO_x (=NO + NO₂), CO₂, H₂, NH₃ and N₂ outlet concentration vs. time. Fig. 8A and C refer to the first cycle over Ag–Ba/CeO₂ and Ag–Sr/CeO₂ catalysts respectively, while Fig. 8B and D refers Fig. 8. Adsorption, reduction and TPO phases over (A and B) Ag–Ba/CeO₂ catalyst; (C and D) Ag–Sr/CeO₂ catalyst in the presence of soot. (A and C): first storage–reduction cycle; (B and D): seventh storage–reduction

cycle and subsequent TPO. Storage phase: 1000 ppm NO + 3% (v/v) O₂ in He at 350 °C; reduction phase: 4000 ppm H₂ in He at 350 °C; TPO in 3% (v/v) O₂ 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 to complete the soot combustion (see Section 2). In the first lean–rich cycle over Ag–Ba/CeO₂ catalyst (Fig. 8A), upon NO and O₂ admission (at t = 0 s) the NO outlet concentration increases with time after a very short NO_x breakthrough (10 s); NO₂ formation is also observed (simultaneously to NO), due to the occurrence of the oxidation of NO by O₂ at Ag sites according to the stoichiometry of reaction (1). The outlet concentrations of both NO and NO₂ increase with time, indicating that the NO_x storage still occurs; worth to note that the storage phase is stopped before a steady state level has been reached. The amounts of NO_x that have been stored onto the catalyst surface are 2.50×10^{-5} mol/gcat, lower than that measured in the absence of soot (9.14×10^{-4} mol/gcat, Fig. 9A), indicating a reduced storage capacity of the catalyst in the presence of soot, as also reported in the literature [32,33,65,66]. A comparison has also been made between the NO_x stored at different residual soot loadings, i.e. in the subsequent lean–rich cycles during soot oxidation, and results are shown in Fig. 9A. It appears that the amount of soot present in the catalyst/soot mixture influences the NO_x storage behavior of the catalytic system. Accordingly, upon decreasing the residual soot loading, the NO_x storage capacity increases, approaching that of the catalyst in the absence of soot, in line with the results over Pt–Ba/Al₂O₃ catalyst and reported by some of us in a previous work [66]. The detrimental effect of the presence of soot on the performances of a Pt–Ba/Al₂O₃ LNT catalyst may be related to the decrease of the NO₂ gas phase concentration, being NO₂ involved in the soot combustion, according to reaction (1): (1) As a matter of fact, the NO/NO₂ value increases from a value near 6 for the soot-free catalyst sample to roughly 15 in presence of soot. In the case of Ag–Ba/CeO₂ catalyst, the NO/NO₂ ratio in the absence and in the presence of soot changes from 1.07 to 2.1 (in the first cycle where the higher amount of soot is present). Therefore, also in this case we can suppose the participation of NO₂ to soot oxidation, even if the decrease in the NO₂ concentration is less evident. Notably, oxidation by NO₂ is not likely the unique pathway for the soot oxidation; the direct participation of active oxygen from ceria and/or silver can also be invoked (as discussed below). Finally, note that reaction (1) may involve the intermediacy of CO although this species has not been observed. In fact, CO may be oxidized to CO₂ by O₂ at Ag sites and/or by NO₂. The storage of NO_x is accompanied by the evolution of CO₂; upon NO admission, the CO₂ 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 NO admission, indicating that soot oxidation occurs also in the presence of O₂ alone. The presence of CO₂ in the outlet gas stream results only from soot oxidation, being CO₂ absent the inlet feed. However, the CO₂ production is not accompanied by the evolution neither of N₂ or N₂O, as reported by some authors [21,22] but $2\text{NO}_2 + \text{C} \rightarrow$

2NO + CO₂ Fig. 9. Total amount of stored NO_x vs. cycle number over (A) Ag–Ba/CeO₂; (B) Ag–Sr/CeO₂ and (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 the Ag–Sr/CeO₂ is much higher with respect to the model Pt–Ba/Al₂O₃, as pointed out by the higher production of CO₂ detected at the reactor outlet in this case (near 1000 ppm vs. near 300 ppm for Pt–Ba/Al₂O₃ [34]). It is worth noting that, upon the NO addition, the production of CO₂ is much higher than that expected from the stoichiometry of reaction (1). This could be explained by considering the possible “NO recycle” mechanism: in fact, similarly to the case of Pt-containing catalysts [67] it may be argued that NO which is formed in reaction (1) may be further oxidized to NO₂ by Ag metallic sites (recycling of NO to NO₂) which could substantially enhance the efficiency of soot combustion. Moreover, as described above, soot combustion is observed even in the absence of NO (i.e. in presence of only oxygen). This suggests a direct role of the catalyst (e.g. direct participation of active oxygen from ceria and/or silver) in the oxidation of soot, which is superimposed to the soot combustion activity by NO₂. Finally, as reported in previous works [32,33,66] a specific role of the stored NO_x species in the soot combustion cannot be excluded, which could contribute to the significant increase in the soot combustion. These routes operate simultaneously in the oxidation of soot, so that the relevance of each pathway cannot be determined. Upon NO shutoff, a release of NO and NO₂ takes place with time due to the desorption of the previously stored NO_x species, and the CO₂ concentration decreases as well. Upon switching off the O₂ feed, other NO_x are also desorbed. Both desorption contributions appear to be remarkable if compared to those observed in Fig. 10. Soot conversion during the lean phase as a function of the cycle number: Ag–Ba/CeO₂ catalyst (thick solid line); Ag–Ba/ZrO₂ catalyst (thin solid line); Ag–Sr/CeO₂ catalyst (dotted line); Pt–Ba/Al₂O₃ catalyst (dashed line). In the soot-free catalyst, suggesting that soot has a destabilizing effect on the NO_x species adsorbed onto the catalytic surface; this behavior is in line with that observed in the case of Pt–Ba/Al₂O₃ LNT catalyst [32,66]. The total amount of NO_x desorbed in the presence and in the absence of soot are near 4.04×10^{-4} mol/g cat and 2.33×10^{-4} mol/g cat, respectively; these values correspond to 94% and 20% of the NO_x adsorbed species present onto the catalytic surface at saturation. This clearly points out to a lower stability of nitrate species in presence of soot. The reduction of the stored NO_x has also been analyzed. Reduction has been carried out at the same temperature (350 °C) by admission of H₂ step (4000 ppm) in He. The results, reported in Fig. 8A in terms of H₂, NO, CO₂ and N₂, NH₃ outlet concentrations as a function of time, point out that the reduction of the NO_x adsorbed species in the presence of soot does not show significant differences with respect to the soot-free catalyst (compare Fig. 6A). Also in this case H₂ is immediately observed at the reactor outlet; its concentration increases with time, reaching the steady state level of inlet concentration. NO represents the main reduction product, along with minor amounts of N₂ and NH₃. No release of other byproducts like N₂O is observed; the selectivity to N₂ is near 45%. The data described above clearly

indicate that the Ag–Ba/CeO₂ catalyst is able to simultaneously store/reduce NO_x and oxidize soot. Considering the whole sequence of the seven NO_x storage–reduction cycles (Fig. 8A and B), it appears that the behavior of the catalytic system is affected by the residual soot loading. Indeed, the NO_x breakthrough progressively increases during the lean/rich sequence (compare Fig. 8A with B) moving from the first to the seventh cycle, respectively, i.e. upon increasing the soot conversion from 27% (w/w) to 85% (w/w). The increase in the deadtime is accompanied by an increase of the amount of NO_x stored during the lean phase, from 2.50×10^{-4} mol/g cat for the first cycle to 7.52×10^{-4} mol/g cat for the seventh cycle (Fig. 9A), near to that of the catalyst in the absence of soot. Note that also the NO/NO₂ ratio changes during soot oxidation, moving from 2.17 in the first cycle to 0.9 in the seventh, very close to the value recorded in the absence of soot (compare Fig. 6A with Fig. 8A and B). Fig. 10 shows the soot conversion during the lean phases as a function of the cycle number, estimated from the amounts of evolved CO₂. In the case of Ag–Ba/CeO₂ catalyst (solid line) during the lean phase of the first cycle, roughly 27% of the initial soot loading (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 loading is near 14% (w/w). In fact, the CO₂ concentration measured at the end of the lean phase decreases from 980 ppm of the first cycle to 70 ppm of the seventh cycle, indicating a progressive decrease of the rate of soot combustion. These results are in line with the data collected on the Pt–Ba/Al₂O₃ LNT catalyst reported in Fig. 10 for comparison purpose. Also in this case, the oxidation of soot takes place progressively during the subsequent lean–rich cycles; however, the oxidation ability of the Pt-based catalyst is much lower than that of the CeO₂-based system, since in the latter case the participation of active oxygen species coming from CeO₂ and/or Ag sites improves the oxidizing performances of the catalytic system. The behavior of Ag–Sr/CeO₂ catalyst in the presence of soot has also been tested and the results are reported in Fig. 8C (first cycle) and D (seventh cycle and TPO). The total amount of stored NO_x vs. cycle number is reported in Fig. 9B, while the conversion of soot during the lean phase as a function of the cycle number is shown in Fig. 10 (dotted line). The results clearly show that the NO_x storage capacity of the Sr-containing catalyst decreases in the presence of soot; the NO_x breakthrough is still zero and the amount of stored NO_x is further decreased by the NO_x desorption at NO and O₂ shut off, so at the end of the first storage phase 1.15×10^{-4} mol/g cat are present at catalyst surface (vs. 7.82×10^{-4} mol/g cat). Moreover, the NO/NO₂ ratio 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/CeO₂ catalyst seems to be independent from the amount of residual soot, i.e. at the end of the seventh cycle the catalyst does not recover its original performance, when more than 60% of soot has been oxidized (see Fig. 10). Also the soot oxidation capability is lower than in case of Ag–Ba/CeO₂ catalyst; indeed, a soot conversion

of 13% is observed in the first cycle increasing up to 74% in the seventh one. Accordingly, the combustion of soot is completed during the subsequent final TPO run. Finally, the effect of soot on the storage capacity has been studied also in the case of Ag–Ba/ZrO₂ catalyst and the results in terms of stored NO_x vs. cycle number are reported in Fig. 9C. The behavior is qualitatively similar to that observed in the case of CeO₂-based catalysts; indeed, the amount of stored NO_x decreases in the presence of soot and the system partially recovers the storage capacity exhibited in the absence of soot only when most of the soot present is burnt. On the other hand, the soot conversion reported in Fig. 10 is lower than that of Ag–Ba/CeO₂ at the beginning and increases up to 90% at the end of the lean–rich sequence.

4. Conclusions

The study focuses on the catalytic behavior of Ag-based catalysts in both soot oxidation and simultaneous removal of soot and NO_x. The results have been compared with that obtained on the reference Pt–Ba/Al₂O₃/LNT catalyst. It has been found that all the Ag-containing catalysts are able to oxidize soot in the presence of NO/O₂ at temperatures near 250 °C, remarkably lower than the uncatalyzed soot oxidation; the presence of Ba or Sr does not significantly affect the catalytic activity. On the other hand, the Ag dispersion improves the oxidation activity, i.e. the catalyst with lower Ag dispersion exhibits higher onset oxidation temperature. All the Ag-containing catalysts are able to simultaneously remove soot and NO_x, when operating under isothermal cycling conditions, i.e. alternating lean–rich phases according to the typical DPNR strategy. The data show that in the absence of soot the storage capacity of the investigated systems is higher than that of traditional Pt–Ba/Al₂O₃/LNT catalyst; however, in the presence of soot, the detrimental effect of soot on the storage capacity is more evident in the case of Ag-based catalysts. The latter are by far more reactive in the soot combustion than the Pt-based catalyst, possibly due to the participation of oxygen active species from ceria and/or silver. In conclusion, the results point out that Ag-based catalysts should be considered as a promising alternative to Pt-based catalysts for the simultaneous removal of soot and NO_x. However, their reactivity in the reduction of the stored NO_x should be further enhanced to improve the N₂ selectivity.

Acknowledgments

The authors thank financial support from MIUR (Futuro in ricerca, FIRB 2012, project SOLYST). J. Llorca is grateful to ICREA Academia program.

References

- [1] A. Russell, W.S. Epling, *Catal. Rev.* 53 (2011) 337–423.
- [2] T.V. Johnson, *Int. J. Engine Res.* 10 (2009) 275–285.
- [3] J.P.A. Neeft, M. Makkee, J.A. Moulijn, *Fuel Process. Technol.* 47 (1996) 1–69.
- [4] B.A.A.L. van Setten, R. van Dijk, S.J. Jelles, M. Makkee, J.A. Moulijn, *Appl. Catal. B: Environ.* 21 (1999) 51–61.
- [5] M.J. Maricq, *Aerosol Sci.* 38 (2007) 1079–1118.
- [6] M.V. Twigg, *Appl. Catal. B: Environ.* 70 (2007) 2–15.
- [7] D. Fino, V. Specchia, *Powder Technol.* 180 (2008) 64–73.
- [8] J.P.A. Neeft, M. Makkee, J.A. Moulijn, *Appl. Catal. B: Environ.* 8 (1996) 57–78.
- [9] N.K. Labhsetwara, M. Dhakada, S.S. Rayalua, R. Kumara, J. Subrtb, H. Hanedac, S. Devotaa, T. Mitsuhashi, *Top. Catal.* 42–43 (2007)

299–302.[10] A.M. Hernández-Giménez, D. Lozano Castelló, A. Bueno-López, *Chem. Pap.* 68(2014) 1154–1168.[11] E. Aneggi, C. de Leitenburg, A. Trovarelli, *Catalysis by Ceria and Related Materials*, vol. 12, 2nd ed., Imperial College Press, 2013, pp. 565–621.[12] A. Bueno-López, *Appl. Catal. B: Environ.* 146 (2014) 1–11.[13] E. Aneggi, C. de Leitenburg, A. Trovarelli, *Catal. Today* 181 (2012) 108–115.[14] M. Machida, Y. Murata, K. Kishikawa, D. Zhang, K. Ikeue, *Chem. Mater.* 20 (2008)4489–4494.[15] E. Aneggi, J. Llorca, C. de Leitenburg, G. Dolcetti, A. Trovarelli, *Appl. Catal. B:Environ.* 91 (2009) 489–498.[16] C. Wen, A.Y. Yin, W.L. Dai, *Appl. Catal. B: Environ.* 160 (2014) 730–741.[17] G. Preda, G. Pacchioni, *Catal. Today* 177 (2011) 31–38.[18] K.-I. Shimizu, H. Kawachi, A. Satsuma, *Appl. Catal. B: Environ.* 96 (2010)169–175.[19] T. Nanba, S. Masukawa, A. Abe, J. Uchisawa, A. Obuchi, *Catal. Sci. Technol.* 2(2012) 1961–1966.[20] G. Corro, U. Pal, E. Ayala, E. Vidal, *Catal. Today* 212 (2013) 63–69.[21] D. Reichert, H. Bockhorn, S. Kureti, *Appl. Catal. B: Environ.* 80 (2008)248–259.[22] K. Krishna, A. Bueno-López, M. Makkee, J.A. Moulijn, *Appl. Catal. B: Environ.* 75(2007) 201–209.[23] J. Suzuki, S. Matsumoto, *Top. Catal.* 28 (2004) 171–176.[24] K. Nakatani, S. Hirota, S. Takeshima, K. Itoh, T. Tanaka, *SAE Paper SP-1674*, 2002-01-0957, 2002.[25] R. Matarrese, L. Castoldi, L. Lietti, P. Forzatti, *Top. Catal.* 52 (2009) 2041–2046.[26] N. Miyoshi, S. Matsumoto, K. Katoh, T. Tanaka, J. Harada, N. Takahashi, K. Yokota, M. Sugiura, K. Kasahara, *SAE Tech. Pap.* (1995) 950809.[27] S. Matsumoto, *Catal. Today* 29 (1996) 43–45.[28] N. Takahashi, H. Shinjoh, T. Iijima, T. Szuki, K. Yamazaki, K. Yokota, H. Suzuki, N. Miyoshi, S. Matsumoto, T. Tanizawa, T. Tanaka, S. Tateishi, K. Kasahara, *Catal.Today* 27 (1996) 63–69.[29] H. Shinjoh, N. Takahashi, K. Yokota, M. Sugiura, *Appl. Catal. B: Environ.* 15 (1998)189–201.[30] L. Lietti, M. Daturi, V. Blasin-Aubé, G. Ghiotti, F. Prinetto, P. Forzatti, *Chem-CatChem* 4 (2012) 55–58.[31] L. Castoldi, R. Matarrese, L. Lietti, P. Forzatti, *Appl. Catal. B: Environ.* 64 (2006)25–34.[32] N. Artioli, R. Matarrese, L. Castoldi, L. Lietti, P. Forzatti, *Catal. Today* 169 (2011)36–44.[33] R. Matarrese, N. Artioli, L. Castoldi, L. Lietti, P. Forzatti, *Catal. Today* 184 (2012)271–278.[34] R. Matarrese, L. Castoldi, L. Lietti, P. Forzatti, *Top. Catal.* 42–43 (2007) 293–297.[35] R. Matarrese, L. Lietti, L. Castoldi, G. Busca, P. Forzatti, *Top. Catal.* 56 (2013)477–482.[36] R. Matarrese, L. Castoldi, N. Artioli, E. Finocchio, G. Busca, L. Lietti, *Appl. Catal. B: Environ.* 144 (2014) 783–791.[37] K. Krishna, M. Makkee, *Catal. Today* 114 (2006) 48–56.[38] A. Setiabudi, M. Makkee, J.A. Moulijn, *Appl. Catal. B: Environ.* 50 (2004)185–194.[39] B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, *Catal. Rev.* 43 (2001) 489–564 [40] M.A. Peralta, M.S. Gross, B.S. Sanchez, C.A. Querini, *Chem. Eng. J.* 152 (2009)234–241.[41] L. Lietti, P. Forzatti, I. Nova, E. Tronconi, *J. Catal.* 204 (2001) 175–191.[42] F. Frola, M. Manzoli, F. Prinetto, G. Ghiotti, L. Castoldi, L. Lietti, *J. Phys. Chem. C*112 (2008) 12869–12878.[43] C. Morterra, G. Magnacca, V. Bolis, G. Cerrato, M. Baricco, A. Giachello, M. Fucale, in: A. Frennet, J.-M. Bastin (Eds.), *Catalysis and automotive pollution control III*, *Stud. Surf. Sci. Catal.* 96 (1995) 361–373.[44] A. Piras, A. Trovarelli, G. Dolcetti, *Appl. Catal. B: Environ.* 28 (2000) L77–L81.[45] X.D. Wu, S.A. Liu, F. Lin, D.A. Weng, *J. Hazard. Mater.* 181 (2010) 722–728.[46] C. Lei, M.Q. Shen, M. Yang, J. Wang,

J. Wang, *Appl. Catal. B: Environ.* 101 (2011)355–365.[47] V.G. Milt, E.D. Banus, E.E. Miró, M. Yates, J.C. Martin, S.B. Rasmussen, P. Avila, *Chem. Eng. J.* 157 (2010) 530–538.[48] T. Nanba, S. Masukawa, A. Abe, J. Uchisawa, A. Obuchi, *Appl. Catal. B: Environ.*123 (2012) 351–356.[49] F. Giordano, A. Trovarelli, C. de Leitenburg, M. Giona, *J. Catal.* 193 (2000)273–282.[50] L. Ilieva, J.W. Sobczak, M. Manzoli, B.L. Su, D. Andreeva, *Appl. Catal. A: Gen.* 291(2005) 85–92.[51] E.P. Reddy, R.S. Varma, *J. Catal.* 221 (2004) 93–101.[52] Z.P. Qu, M.J. Cheng, W.X. Huang, X.H. Bao, *J. Catal.* 229 (2005) 446–458.[53] N. Gungor, S. Isci, E. Gunister, W. Mista, H. Teterycz, R. Klimkiewicz, *Appl. ClaySci.* 32 (2006) 291–296.[54] Z.P. Qu, M.J. Cheng, X.L. Dong, X.H. Bao, *Catal. Today* 93–95 (2004) 247–255.[55] G.I.N. Waterhouse, G.A. Bowmaker, J.B. Metson, *Appl. Surf. Sci.* 214 (2003)36–51.[56] A.J. Nagy, G. Mestl, D. Herein, G. Weinberg, E. Kitzelmann, F. Schlogl, *J. Catal.*182 (1999) 417–429.[57] L. Kundakovic, M. Flytzani-Stephanopoulos, *Appl. Catal. A: Gen.* 183 (1999)35–51.[58] M. Machida, Y. Murata, K. Kishikawa, D.J. Zhang, K. Ikeue, *Chem. Mater.* 20(2008) 4489–4494.[59] J. Oi-Uchisawa, A. Obuchi, R. Enomoto, J.Y. Xu, T. Nanba, S.T. Liu, S. Kushiya, *Appl. Catal. B: Environ.* 32 (2001) 257–268.[60] B.J. Cooper, S.A. Roth, *Platin. Met. Rev.* 35 (1991) 178–187.[61] L. Castoldi, I. Nova, L. Lietti, P. Forzatti, *Catal. Today* 96 (2004) 43–52.[62] I. Nova, L. Castoldi, L. Lietti, E. Tronconi, P. Forzatti, F. Prinetto, G. Ghiotti, *J. Catal.*222 (2004) 377–388.[63] W.S. Epling, L.E. Campbell, A. Yezerets, N.W. Currier, J.E. Parks II, *Catal. Rev.* 46(2004) 163–245.[64] I. Nova, L. Castoldi, L. Lietti, E. Tronconi, P. Forzatti, *Top. Catal.* 42–43 (2007)21–25.[65] J.A. Sullivan, O. Keane, A. Cassidy, *Appl. Catal. B: Environ.* 75 (2007) 102–106.[66] L. Castoldi, N. Artioli, R. Matarrese, L. Lietti, P. Forzatti, *Catal. Today* 157 (2010)384–389.[67] S.J. Jelles, R.R. Krul, M. Makkee, J.A. Moulijn, *Catal. Today* 53 (1999)623–630.