NEW FOUR-WAY SILVER- AND RUTHENIUM-BASED CATALYSTS FOR NO\textsubscript{X} AND SOOT REMOVAL. PART II


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Abstract
The paper presents the main results achieved during the three years-SOLYST project. The objective of this project was to develop a new generation of catalytic converters for pollutants emissions from vehicles, through the fundamental understanding of the multiphase particulate-gas-catalyst interactions. Four research groups have been involved in the project: Politecnico di Torino, Università di Udine, Politecnico di Milano and IRC-CNR di Napoli. The Politecnico di Milano Research Unit was mainly involved in the testing of the innovative catalytic materials for storage-reduction NO\textsubscript{x} applications (LNT) and for simultaneous removal of NO\textsubscript{x} and soot (DeNO\textsubscript{x} - DeSoot). Silver- and ruthenium-based catalysts have been prepared and fully characterized by the Università di Udine Research Unit (see abstract part I). Here, they are investigated for the simultaneous removal of particulate matter (soot) and NO\textsubscript{x} and their behavior is compared with that of model DPNR catalysts. The catalytic activity for diesel soot combustion, in loose contact conditions, has been studied by means of TPO experiments while NO\textsubscript{x} removal is investigated through NO\textsubscript{x} storage-reduction cycles. Both the Ag- and Ru-based formulations result active in the soot oxidation, more than the traditional Pt-containing DPNR catalyst. Besides, the Ru-based samples show remarkable performances in the DeNO\textsubscript{x} - DeSoot activity, although their activity in the reduction step of the stored NO\textsubscript{x} still needs further improvements.

Introduction
The new stringent regulation limits (EURO 6) on the nitrogen oxides (NO\textsubscript{x}) and soot emissions are forcing to develop innovative catalytic systems that combine denitrification catalysts (such as NO\textsubscript{x} adsorption/reduction catalysts, LNT) with catalytic filters. The DPNR (Diesel Particulate-NO\textsubscript{x} Reduction) technology [1] has been proposed to remove simultaneously soot and NO\textsubscript{x}. The soot combustion is accomplished on LNT (Lean NO\textsubscript{x} trap) catalysts. These catalytic systems work under cyclic conditions, alternating a lean phase during which NO\textsubscript{x} are adsorbed on the alkaline or alkaline-earth metal oxide component, and a short rich phase, during which the stored nitrate species are reduced to nitrogen thanks to noble metals. Soot abatement occurs mainly under lean conditions thanks to the NO\textsubscript{x} and oxygen.

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in the exhaust gas; soot removal is however claimed to occur during the rich phase as well [1]. In previous works, Pt-based LNT catalysts have been investigated in the simultaneous removal of soot and NO\textsubscript{x}, giving satisfactory results [2]. More recently, the combustion of soot was shown to be efficiently promoted by silver and Ru [3,4]. Accordingly, Ag- and Ru-based catalysts supported over CeO\textsubscript{2}, ZrO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3} have been investigated in the DeNO\textsubscript{x} and DeSoot reaction using Ba, Sr and K as storage components and a comparison has been carried out with model Pt-Ba(K)/Al\textsubscript{2}O\textsubscript{3} LNT formulations. The reactivity of Ru-containing samples has also been addressed, in view of the potentiality of this species in the DeNO\textsubscript{x} and DeSoot reactions.

Materials and Methods
Homemade Ag-Ba(Sr)/M\textsubscript{x}O\textsubscript{y} (5/10/100 w/w) and Ru-Ba(K)/M\textsubscript{x}O\textsubscript{y} (1/10/100 w/w), with M\textsubscript{x}O\textsubscript{y} = CeO\textsubscript{2}, ZrO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, have been prepared by impregnation of the selected support with aqueous solutions of silver nitrate, ruthenium nitrosyl nitrate, barium acetate or strontium (potassium) nitrate. The catalysts have been characterized by BET, XRD and HRTEM.

The catalytic activity has been investigated in the soot combustion and in the simultaneous removal of soot and NO\textsubscript{x}. Starting from soot/catalyst loose mixtures, and using a model soot (Printex U, Degussa AG), soot oxidation has been carried out by TPO in O\textsubscript{2} (3% v/v) + CO\textsubscript{2} (1000ppm) + H\textsubscript{2}O (1% v/v) in the range 50°C - 750°C (10°C/min). The catalysts have been tested at first in the DeNO\textsubscript{x} activity (in the absence of soot) and then in the simultaneous DeNO\textsubscript{x} – DeSoot activity (in the presence of soot). Both the experiments have been performed at 350°C, by alternating rectangular step feeds of NO (1000ppm) in He + 3% v/v O\textsubscript{2} (lean phase) and of hydrogen (4000 ppm) in He (rich phase), separated by a He purge in between.

Results and Discussion
Catalyst characterization – CeO\textsubscript{2} and ZrO\textsubscript{2} support exhibit a surface area near 50-60 m\textsuperscript{2}/g, while the Al\textsubscript{2}O\textsubscript{3} shows a value near 130 m\textsuperscript{2}/g. The addition of metal and alkaline(-earth) oxides slightly decreases these values. All the catalysts have been characterized by XRD analysis. In the case of Ag-based catalysts, X-ray diffraction profiles show the formation of metallic Ag, while in the case Ru-based samples, no evidence of the presence of ruthenium crystallites (metallic or oxide) was obtained. Barium (Sr, K) carbonate peaks were also detected, along with peaks belonging to the supports (CeO\textsubscript{2}, ZrO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}). For more characterization information see abstract part I.

TPO experiments - The results of TPO runs carried out over Ag- and Ru-based catalysts are reported in Fig. 1; traditional Pt-Ba/Al\textsubscript{2}O\textsubscript{3} and Pt-K/Al\textsubscript{2}O\textsubscript{3} LNT catalysts are also reported for comparison purpose.
All the investigated catalysts are active in the soot oxidation with a remarkable decrease of oxidation onset temperature compared to uncatalyzed reaction; the catalytic oxidation is highly selective to CO$_2$ (only negligible amount of CO were formed), whereas the uncatalyzed reaction produces CO along with CO$_2$.

Both the Ag- and Ru-based catalysts show onset temperatures lower than those of the Pt-based materials. Among all the investigated formulations, Ru-based catalysts resulted to be particularly active. RuBa-based catalysts exhibit onset temperatures for soot combustion near 350°C, compared to 400°C and 480°C found over AgBa- and PtBa-catalysts, respectively (compare Fig. 1A and 1B). The substitution of Ba with Sr in the Ag/Ce catalyst does not have significant effect, while the substitution of Ba with K in the Ru-based catalysts further decreases the onset temperature of soot oxidation to ca. 300°C (Fig. 1B). The relatively high activity of the Ag-containing sample is likely related to the ability of metallic silver to form several sub-oxide species and/or superoxide O$_2^-$ ions under oxidative atmosphere [5]. Similarly, the high oxidation activity of Ru-based materials should be related to the dissociative adsorption of O$_2$ on catalyst surface followed by its reaction with the solid carbon/soot.

**DeNO$_x$ activity** - The DeNO$_x$ (i.e. the removal of NO$_x$) activity has been tested at first. The catalytic materials that have been considered in this phase are the CeO$_2$-supported silver catalysts, namely Ag-Ba/CeO$_2$ and Ag-Sr/CeO$_2$, in order to elucidate the role of the storage component (i.e. of the alkaline-earth metal oxide, Ba vs. Sr). Then in the case of Ba-containing catalysts, the effect of the support (i.e. CeO$_2$ vs. ZrO$_2$ and Al$_2$O$_3$) has been studied as well. In the Ru-based family catalysts, Ru-Ba and Ru-K supported on Al$_2$O$_3$ or ZrO$_2$ have been considered, in order to elucidate both the role of the support and of the storage component.
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**Figure 2.** Adsorption, reduction and thermal desorption phases over A) Ag-Ba/Al₂O₃; B) Ru-Ba/Al₂O₃ in the absence of soot. Storage phase: 1000 ppm NO + 3% v/v O₂ in He at 350°C; reduction phase: 4000 ppm H₂ in He at 350°C

Fig. 2A and 2B show the results of a typical lean-rich cycle at 350°C over fully conditioned Ag-Ba/Al₂O₃ and Ru-Ba/Al₂O₃ catalysts, as representative of the general behavior of the two catalysts families. Upon NO admission, both the Ag and Ru-containing systems show a significant dead time for NO₃ breakthrough. Then the NO₃ concentration gradually increase up to steady state. A significant NO to NO₂ oxidation is also observed, particularly in the case of the Ru-based catalyst sample. At the end of adsorption, upon decreasing the NO and O₂ partial pressure, a tail is observed in the NO₃ concentration, particularly in the case of Ru-Ba/Al₂O₃ catalyst. The tail is related to the release of weakly adsorbed species; in the case of the Ru-based sample a NO₃ desorption peak is also observed upon decreasing the O₂ concentration (arrow in Fig. 2). These data indicate that, at variance with that observed in the case of the Ag- (and Pt-) based catalysts, a significant fraction of NO₃ species stored onto the Ru-based catalyst shows poor stability In Fig. 3 the integral curves of stored NO₃ versus time for the various investigated samples are reported together with that of Pt-Ba/Al₂O₃ model LNT catalyst.

**Figure 3.** Integral curves of stored NO₃ versus time over Ag- and Ru-based catalysts, and Pt-Ba/Al₂O₃ model LNT catalyst for comparison purpose.
The Pt-Ba/Al₂O₃ catalyst exhibits a lower storage capacity than that of the two CeO₂-supported catalysts; in particular, the amount of stored NOₓ increases in the order Pt-Ba/Al₂O₃ < Ag-Sr/CeO₂ < Ag-Ba/CeO₂. The CeO₂-supported catalyst shows higher storage capacity than ZrO₂- and Al₂O₃-supported systems; those in turn exhibit a lower storage capacity with respect to the traditional Pt-based LNT catalyst. The storage capacity in Ru-containing catalyst is lower than that of model Pt-Ba/Al₂O₃ LNT catalyst. After NO adsorption and He purge, the subsequent NOₓ reduction has been performed with admission of H₂ to the reactor (Fig. 2, right side of the panels). In the case of the Ag-containing sample, NO is the main reduction product as clearly appears from the inset of Fig. 2A; accordingly, the selectivity to N₂ is poor, near 30%. On the other hand, in the case of the Ru catalyst, formation of N₂ is mainly observed, with a rather high N₂ selectivity, near 90%. Notably, in both cases the reduction of the stored NOₓ is not complete, as pointed out by a subsequent thermal desorption up to 500°C (not shown) that allowed the complete removal of the stored NOₓ species. At variance, over the alumina supported Pt-based catalyst, the reduction of the stored NOₓ is almost complete.

**DeNOₓ-DeSoot activity** – All the prepared catalysts have been tested in the simultaneous removal of NOₓ and soot. The best performances in terms of soot combustion, NOₓ storage capacity in the presence of soot and N₂ selectivity in the reduction of stored NOₓ have been shown by Ru-Ba/Al₂O₃ catalyst; for this reason, only the results related to this catalytic system have been here reported. Sequential lean-rich cycles have been performed at 350°C over the Ru-Ba/Al₂O₃/soot mixture until almost complete soot oxidation. The soot oxidation starts already upon O₂ admission at 350 °C before NO admission (data not reported for brevity), as confirmed by the evolution of small amounts of CO₂. Then, upon NO admission, the NO outlet concentration increases with time showing a dead time for NOₓ breakthrough near 200s, accompanied by NO₂ formation as well, due to the occurrence of the oxidation of NO by O₂ at Ru sites. The storage of NOₓ is accompanied by a significant evolution of CO₂, due to soot oxidation. Fig. 4 shows the soot conversion (estimated from the CO₂ evolution) and the amounts of stored NOₓ measured in the various lean-rich cycles.

![Figure 4. Soot conversion and stored NOₓ on Ru-Ba/Al₂O₃ in the subsequent 7 lean-rich cycles during soot oxidation](image-url)
As shown in the Fig. 4, roughly 90% of the initial soot content is consumed during the initial four cycles, indicating a very high activity in the soot combustion. The amounts of stored NO\textsubscript{x} is not greatly affected by the presence of soot: in fact during the various cycles it remain constant and it is near the value measured in the case of the soot-free sample; during the first cycle even an higher amounts of NO\textsubscript{x} could be stored on the catalyst. Accordingly, for this catalyst any detrimental effect due to the presence of soot has been observed, at variance to the traditional Pt-based LNT catalysts.

Main Conclusions
The Ag- and Ru-based catalysts investigated in this study are able to oxidize soot in the presence of O\textsubscript{2} at temperatures near 350–400 °C, remarkably lower if compared to the uncatalyzed soot oxidation and to the model Pt-containing sample. In particular, the Ru-based catalyst is by far more active in the soot combustion than the Pt-based catalyst, possibly due to the participation of oxygen active species from ruthenium. Both the Ag- and Ru-containing catalysts are also able to remove NO\textsubscript{x}, when operating under isothermal cycling conditions according to the typical DPNR strategy. In the presence of soot, Ru-Ba/Al\textsubscript{2}O\textsubscript{3} does not suffer of the detrimental effect of soot on the storage capacity that was significant in the case of Pt-based catalysts. In conclusion, the results point out that Ru-based catalyst should be considered as a promising alternative to Pt-based catalysts for the simultaneous removal of soot and NO\textsubscript{x}. However, their reactivity in the reduction of the stored NO\textsubscript{x} should be further enhanced to improve the N\textsubscript{2} selectivity.

References

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