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“CATALYSIS: FUNDAMENTALS AND APPLICATIONS”

Development of PGM-Free Catalysts  
for Automotive Applications<sup>1</sup>

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**Abstract**—The activity of Ag-based catalysts in soot oxidation using  $\text{NO}_2$  and oxygen as oxidants has been characterized in laboratory tests (TGA) and under real conditions on an engine dynamometer. Under low-temperature  $\text{NO}_2$ -assisted and high-temperature  $\text{O}_2$ -assisted soot oxidation conditions, the activity of Ag-based catalysts was found to be comparable or higher than that of commercial Pt-catalysts. In addition, Ag-based compositions also revealed noticeable  $\text{NO}_x$  storage, some passive  $\text{NO}_x$  reduction ability, and activity in NO oxidation. Ag-catalysts characterized in the present paper may be promising for the retrofit applications and high-temperature periodical regenerations with air for diesel passenger cars.

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## 1. INTRODUCTION

High and steadily increasing prices for the Platinum Group Metal (PGM) components of automotive catalysts coupled with limited supply and high demand put a pressure on automakers to reduce PGM loading and replace costly PGM components [1]. This is especially important for diesel aftertreatment, where current PGM loadings are significantly higher than for petrol engines. Diesel aftertreatment is more complicated in general due to the lower temperatures, higher level of sulfur in fuel, and the presence of soot (particulate matter, PM).

At the moment, typical Euro 4/Euro 5 diesel aftertreatment systems include two monolithic devices: the diesel oxidation catalyst (DOC) and the diesel particulate filter (DPF), both having reasonably high Pt loading. The DOC is designed to reduce hydrocarbon (HC) and CO emissions and to rise the temperature when needed for DPF regeneration from soot (by combusting injected fuel), while the DPF collects soot by wall-through filtration and has to be regenerated periodically to oxidize collected PM. To be compliant with Euro 5/6 emission legislation, an additional  $\text{NO}_x$  aftertreatment device may be required, either a lean  $\text{NO}_x$  trap (LNT) or a selective catalytic reduction (SCR) catalyst using  $\text{NO}_x$  reduction with ammonia. SCR catalysts are PGM free, while for the current LNT catalysts, high Pt loadings and also more costly Rh are used. Our research was focused on studying the following problems:

(1) Continuous DPF regeneration via  $\text{NO}_2$ -assisted soot oxidation on Ag and Co-based catalysts;

(2) Periodical high-temperature mainly oxygen-assisted DPF regeneration on low-PGM-base metal and PGM-free Ag–CuO catalysts;

(3)  $\text{NO}_x$ -adsorption and reduction properties of Ag- and Co-based catalysts.

## 2. EXPERIMENTAL

All catalysts were prepared using the so-called “wetness impregnation method.” The fine powder from the filter substrate SiC or cordierite was in service for laboratory testing, and full-size monolithic filters made from SiC or cordierite were in service for engine testing. The filter or powder was impregnated with a solution containing nitrates of active metal components, as an example silver and copper nitrate, with the addition of citric acid. For  $\text{NO}_x$  study, the core samples 1" D × 1.5" L (1 inch in diameter and 1.5 inches in length) were drilled from flow-through monoliths made from cordierite, which was preliminary washcoated with alumina. The core samples were then impregnated with a silver nitrate solution. More detailed information on preparation can be found in [2, 5, 6, 8].

Reference PGM-containing prototypes for DPFs were supplied from three different companies, and here they are marked as samples A, B, and C, commercial DOC and LNT were also tested for  $\text{NO}_x$  study for comparison purposes. Uncoated DPFs made from SiC or cordierite were also tested for comparison purposes. All filters had a standard size 5.66" D × 6" L and 2.5 L volume. Cahn 2000 TGA and Hiden IGA-003 analyzer equipped with mass-spectrometer was used for thermogravimetric soot oxidation study. The reaction mixture was 6, 8, or 10%  $\text{O}_2$  in  $\text{N}_2$ . The catalyst deposited on fil-

<sup>1</sup> The text was submitted by the authors in English.

ter substrate material was mixed with soot by spatula. Real diesel soot was used; for some experiments we also used FW2 soot from Degussa which had properties very close to diesel soot. For continuous regeneration, the filters of 5.66" D  $\times$  6" L were tested on an engine dynamometer with a Ford 1.8 L engine equipped with a commercial DOC in a close-coupled position. Euro 3 (350 ppm S) and Euro 4 (50 ppm S) fuels were used for comparative tests. The testing protocol included the following steps:

- (i) High-temperature cleaning of the DPF;
- (ii) Soot loading at moderate pre-DPF temperatures (ca. 225°C) and soot loading rate of about 4 g/h;
- (iii) Ramp regeneration performed at 2000 rpm by increasing the engine load from 30 to 150 N m to get the pre-DPF temperature increase from 200 to 450°C holding 15 min at each temperature with switched off EGR (exhaust gas recycling).

For periodical high-temperature regenerations, a 2.0 L Ford CR Turbo Diesel engine was used with standard DOC installed upstream of a DPF. The experimental sequence included the following tests:

- (i) Initial steady-state regeneration was performed at constant temperature (about 550°C);
- (ii) The number of severe (drop-to-idle, DTI) regenerations were carried out with soot loading increased from test to test with an increment of about 2 g/L. These DTI regenerations were initiated by increasing the pre-DPF temperature up to about 600°C, followed by switching the engine into idling, 900 rpm.
- (iii) Final steady-state regeneration was performed at about 550°C.

For laboratory testing, the mixtures of soot and catalysts were tested in a quartz flow reactor under a reaction mixture of 10% O<sub>2</sub> in N<sub>2</sub>. The reactor effluent gases were analyzed using an electrochemical analyzer and standard GC. The core catalysts for NO<sub>x</sub> study were tested in a laboratory flow reactor. Reactor effluents were analyzed with a GC. NO and NO<sub>2</sub> content was measured continuously with an Eco-Physics NO/NO<sub>x</sub> analyzer.

To study NO<sub>x</sub> storage/conversion properties, alternating lean (60 s)/rich ( $\lambda = 0.9$ ; 10 s) conditions were used; such L/R cycling was repeated until steady-state NO<sub>x</sub> conversion was obtained. Lean and rich mixtures were supplied using separate lines equipped with mass-flow controllers and high-speed solenoid valves; the switching between lean and rich reaction mixtures was performed automatically and controlled by computer software.

NO and NO<sub>2</sub> adsorption capacity was measured using the reaction mixture: NO or NO<sub>2</sub>—750 ppm, CO<sub>2</sub>—5%, H<sub>2</sub>O—5%, O<sub>2</sub>—10%, N<sub>2</sub>—balance. Adsorption isotherms were measured at 100–350°C with 50°C steps. TPD study was performed after each adsorption experiment with a selected temperature

ramp of 10 K/min using the same reaction mixture except NO up to 600°C.

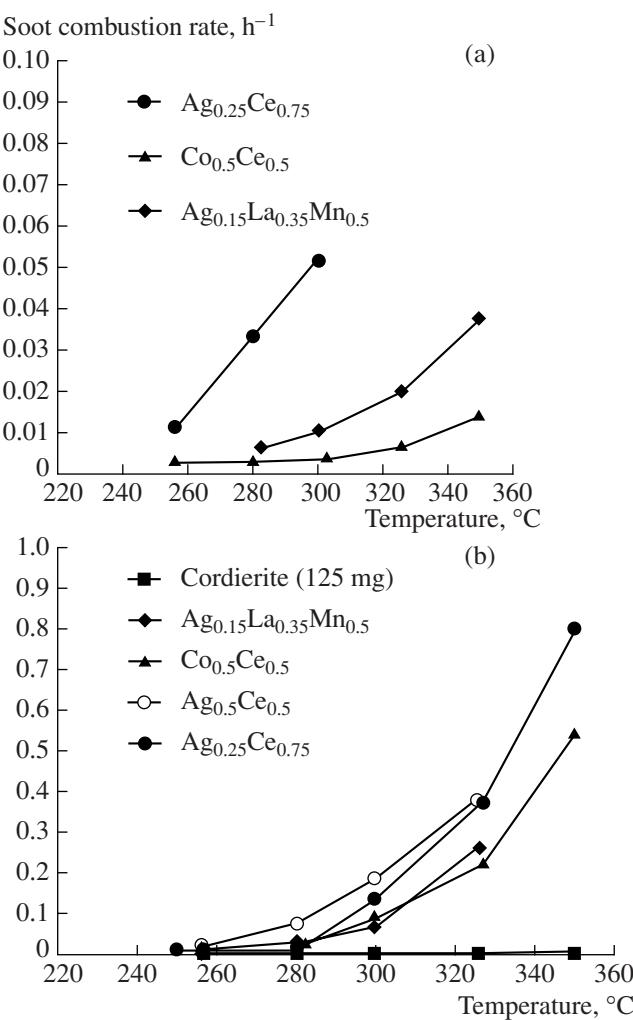
NO oxidation activity was evaluated under the same reaction mixture as for NO adsorption experiments. The NO conversion to NO<sub>2</sub> was measured after reaching the steady-state conversion at different temperatures with 25°C steps.

### 3. RESULTS AND DISCUSSION

#### 3.1. Continuous NO<sub>2</sub>-Assisted Soot Oxidation on Ag- and Co-Based Catalysts

The PGM-free catalytic compositions comprising silver and/or cobalt stabilized ceria facilitating soot oxidation during the regeneration of DPFs replacing PGM formulations are described in [2]. The catalysts were studied by the TGA method on soot oxidation activity. The catalyst and soot were mixed with a spatula, imitating so-called “loose contact,” which is typical for soot oxidation on a DPF [3]. Among the formulations tested, the silver-stabilized ceria and cobalt-stabilized ceria formulations can oxidize soot at 250–350°C in the presence of NO<sub>2</sub> and oxygen, while silver–ceria can slowly oxidize diesel soot even in the presence of only oxygen at these temperatures. The data are presented in Fig. 1. The oxidation is very slow using oxygen (Fig. 1a), requiring hours for significant conversion, but the rate of soot oxidation can be increased significantly by the addition of NO<sub>2</sub>. The synergetic effect between silver and ceria is remarkable, because pure silver and ceria were practically not active in soot oxidation below 400°C. The composition Ag–La–Mn with perovskite structure was very active in soot oxidation at temperatures above 300°C.

Silver and cobalt/ceria catalysts were then deposited on DPFs and were tested under real engine conditions together with uncoated filter and platinum-containing reference prototypes, having Pt loading 100 g/ft<sup>3</sup> (28.3 g Pt/m<sup>3</sup>). The results for passive continuous regeneration using NO<sub>2</sub> emitted from the engine are shown in Fig. 2. The bare (uncoated) filter has shown a nonlinear and fast increase of pressure drop ( $\Delta P$ ) during preliminary soot loading, indicating soot deposition on the filter, while Pt-containing prototypes and prepared PGM-free filters had a lower and linear increase of pressure drop due to the slow soot oxidation even under loading conditions, and this increase was lower for Ag/Ce and Co/Ce catalysts, as can be seen in Fig. 2a. For these PGM-free DPFs, regeneration efficiencies and rates of soot oxidation were also comparable to or better than that of Pt-containing DPFs, as is shown in Fig. 2b. The balance point temperature (i.e., the temperature at which, under given conditions, the rates of soot deposition and oxidation are equal, so that there was no further pressure drop increase) was obtained at 250–275°C, while complete soot oxidation was observed at about 325°C. The Ag/CeO<sub>2</sub> catalyst revealed the best performance and had the lowest  $\Delta P$  at all studied tem-

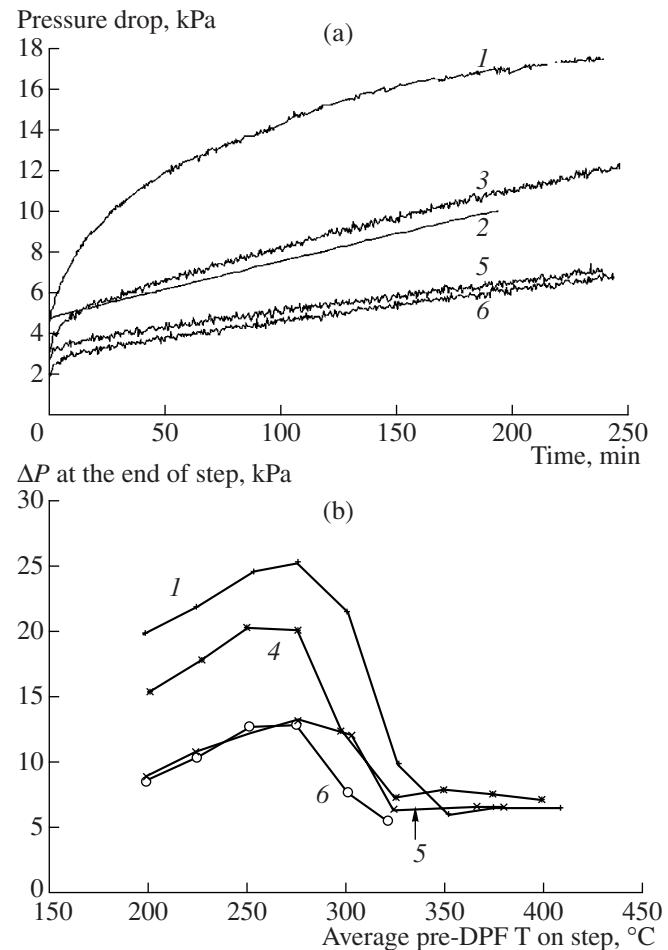


**Fig. 1.** Comparison of soot oxidation rates on Ag and Co-based catalysts in 10% O<sub>2</sub>–N<sub>2</sub> (a) and 10% O<sub>2</sub>–1010 ppm NO<sub>2</sub>–N<sub>2</sub> (b) reaction mixtures. Conditions: 25 mg of catalyst to 20 mg of diesel soot, except for Blanc cordierite 125 mg. Gas flow 50 ml/min. Normalized rate of soot oxidation,  $r = d(M/M_0)/dt$  [1/h], where  $M$  is soot mass and  $M_0$  is the initial soot mass.

peratures, while Co/CeO<sub>2</sub> revealed soot oxidation properties comparable to Pt-containing commercial prototypes.

### 3.2. Soot Oxidation Using High-Temperature Periodical Regeneration with Oxygen on Low-PGM and PGM-Free Ag–CuO Catalysts

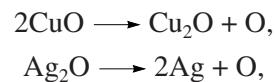
However, such passive filter regeneration with NO<sub>2</sub> assistance is in service only for heavy-duty applications, e.g., trucks, buses, and commercial vehicles, and it is quite difficult for passenger cars due to the lower temperatures and lower level of nitrogen oxides; in addition, the regeneration with NO<sub>2</sub> leads to a high NO<sub>x</sub> penalty. For passenger diesel cars, the automakers can rely only on periodical high-temperature regeneration above 550°C using active engine measures and intake

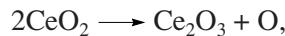


**Fig. 2.** Pressure drop increase during soot loading (a) and the pressure drop decrease during regeneration (b) on catalyzed and uncoated DPFs: (1) uncoated filter, (2) commercial sample A, (3) commercial sample B, (4) commercial sample C, (5) Co/CeO<sub>2</sub>, and (6) Ag/CeO<sub>2</sub>. Engine bench: 1.8 L CR Ford Diesel engine. Soot loading at 225°C. Sulfur level 350 ppm in fuel. Balance point test: 2000 rpm, load 30–150 Nm in 25°C steps 15 min each. Ag/CeO<sub>2</sub> and Co/CeO<sub>2</sub> catalyzed DPF vs. reference Pt-containing DPFs with Pt loading 100 g/ft<sup>3</sup>.

air as an oxidant [1]. The regeneration of a filter for this type of regeneration is quite complicated and requires an active regeneration strategy to increase the exhaust temperature up to 600–650°C. Soot and the catalyst are two solids, and the contact between the catalyst deposited on the filter and the soot is loose or is not available. One approach to solve this problem is to use the catalysts with high mobility originating from their low melting temperature or to use volatile catalysts [3, 4]; however, such catalysts are not practical for automotive applications.

We have focused on another opportunity to obtain active oxygen forms which may be released from the oxide matrix:





In the case of metallic silver, this active oxygen can be generated also from subsurface oxygen. Unfortunately, the gas-phase oxygen typically suppresses the release of matrix oxygen up to high temperatures, while we always have an excess of oxygen under diesel conditions.

Using TGA screening, we have found that under the “loose” contact conditions, only the oxides of copper, silver, and chromium, when deposited on ground filter material, were really active below 600°C. Other metal oxides including transition metals and ceria were practically not active. Especially good activity was found for mixed Cu-La oxide ( $\text{La}_2\text{CuO}_4$ ) with the perovskite-like structure of the  $\text{K}_2\text{NiF}_4$  type and its mixture with copper oxide. The results of soot oxidation in flow reactor are presented in the table.

For the  $\text{CuO}-\text{La}_2\text{CuO}_4$  catalyst, we observed that the activity in soot oxidation was close to that of the  $\text{Pt}/\text{CeO}_2$  catalyst, which models a number of commercial soot oxidation compositions. The most interesting was however the good synergy found between the noble metal component Pt, Pd, Pt-Pd, or Ag and this copper-containing compound, thus leading to better performance relative to individual components in soot oxidation.

Based on this synergy, new catalytic compositions containing very low (5–15 g/ft<sup>3</sup>) Pt, Pd, or Pt-Pd loading in combination with the  $\text{CuO}-\text{La}_2\text{CuO}_4$ -based oxide and PGM-free Ag–CuO–La<sub>2</sub>CuO<sub>4</sub> compositions were developed [5].

These in-house prepared compositions were evaluated on an engine using an active regeneration strategy and compared with Pt-containing prototypes having higher Pt loading. The results can be seen in Fig. 3. Surprisingly, the commercial prototypes were not really active in soot oxidation, providing the same temperature of soot ignition as uncoated DPF, as presented in Fig. 3a. Here the soot ignition temperature was defined as the temperature at which, due to the initiation of regeneration, the pressure drop reaches its maximum in time (i.e., the point at which  $dP/dt = 0$ ). Commercial prototypes had unexpectedly worse soot regeneration properties at low mass soot loadings than uncoated DPF, but were very active at high soot loading, as one can see in Fig. 3b. The reason is effective CO oxidation observed on Pt-containing DPFs, leading to huge additional heat release and propagation of soot combustion at high soot loadings with extremely high peak temperatures during drop-to-idle regenerations (DTIRs). These features of Pt-containing DPFs are presented in Figs. 4b (high peak temperatures) and 4d (activity in CO oxidation). Those DTIRs are the “worst case scenario” for filter regeneration that can occur in real life with high oxygen and limited flow through the DPF leading to the highest peak temperatures. The peak tem-

Table

| Sample                                     | $T_{10}$ , °C | $T_{50}$ , °C | $T_{90}$ , °C |
|--|---------------|---------------|---------------|
| Cu–Co (spinel)                             | 490           | 558           | 610           |
| Pt/CeO <sub>2</sub>                        | 458           | 542           | 593           |
| Pd/CeO <sub>2</sub>                        | 472           | 563           | 611           |
| Ag/CeO <sub>2</sub>                        | 473           | 560           | 610           |
| CuO–La <sub>2</sub> CuO <sub>4</sub> (CLC) | 457           | 532           | 592           |
| Pt–CLC                                     | 458           | 526           | 578           |
| Pd–CLC                                     | 438           | 511           | 568           |
| Ag–CLC                                     | 438           | 519           | 578           |
| CuO  | 457           | 545           | 602           |
| Cu–Ce–Fe                                   | 465           | 543           | 600           |
| Pt–CoLaO <sub>3</sub> (perovskite)         | 470           | 546           | 592           |

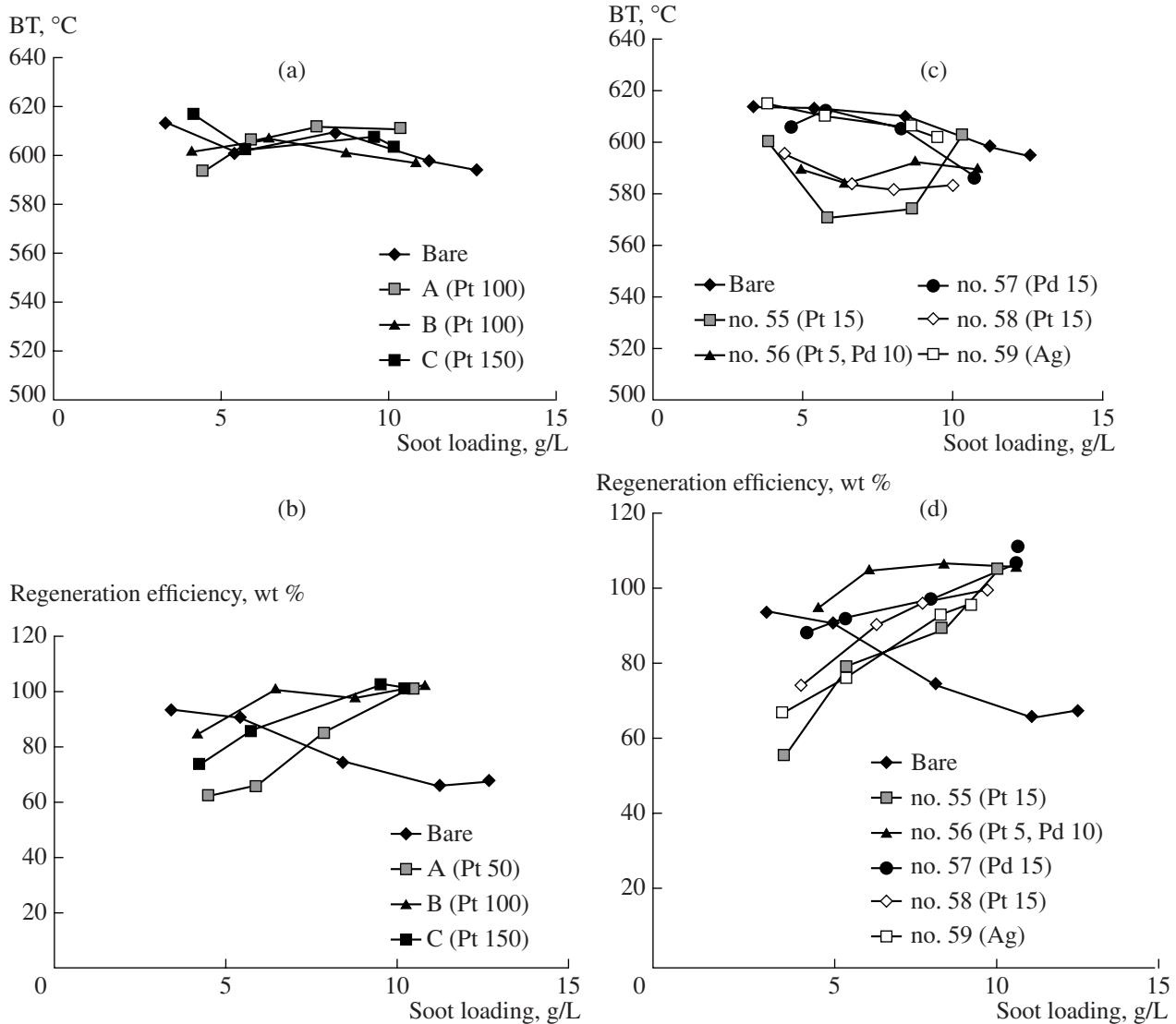
Note: Soot oxidation properties of different catalysts in the flow reactor. 40 mg of catalyst and 10 mg of diesel soot. Gas flow 30 ml/min under reaction mixture 10% O<sub>2</sub>–N<sub>2</sub>. Temperature ramp 10°C/min. Catalysts were prepared on alumina-wash-coated ground SiC powder and were preliminary calcined at  $T = 750^\circ\text{C}$  16 h before the testing.  $T_{10}$ ,  $T_{50}$ , and  $T_{90}$  are the temperatures of 10, 50, and 90% soot conversion, correspondingly.

peratures exceeded 1200°C for Pt-coated commercial prototypes even at 9–10 g/L soot loading, as can be seen in Fig. 4b, melting or destroying the filters. As a result, the maximal possible soot loading was 3–4 g/L lower than for bare DPF.

In contrast, some in-house prepared low-PGM DPFs displayed activity in soot ignition despite the lower PGM loading, as presented in Fig. 3c and we observed excellent soot regeneration properties for some noble metal–base metal oxide combinations. The best was the Pt and Pt-Pd combination with copper–lanthanum metal oxide, as shown in Figs. 3c and 3d. All compositions were prepared on preliminary alumina-washcoated filters made from SiC.

Catalyzed DPF with PGM-free Ag-containing composition had a performance comparable to that of Pt-containing commercial prototypes, but the ignition temperature was practically the same as for the bare filter and higher than for other in-house prepared DPFs, as presented in Fig. 3c, and we observed some deactivation after DTIR regenerations during the last steady-state DPF regenerations at 550°C. In addition, silver and copper oxide loading was too high.

Further investigation has shown that when alumina and lanthanum oxide washcoat components were not used in the catalyst composition, and we directly impregnated uncoated filter material with the solution of silver and copper nitrates, the activity increased remarkably. In this case the low catalyst loading was sufficient to provide a good soot oxidation performance. Based on this result, it was suggested that a thin catalyst layer on the DPF wall (i.e., at a very low catalyst loading) can provide much better interaction with

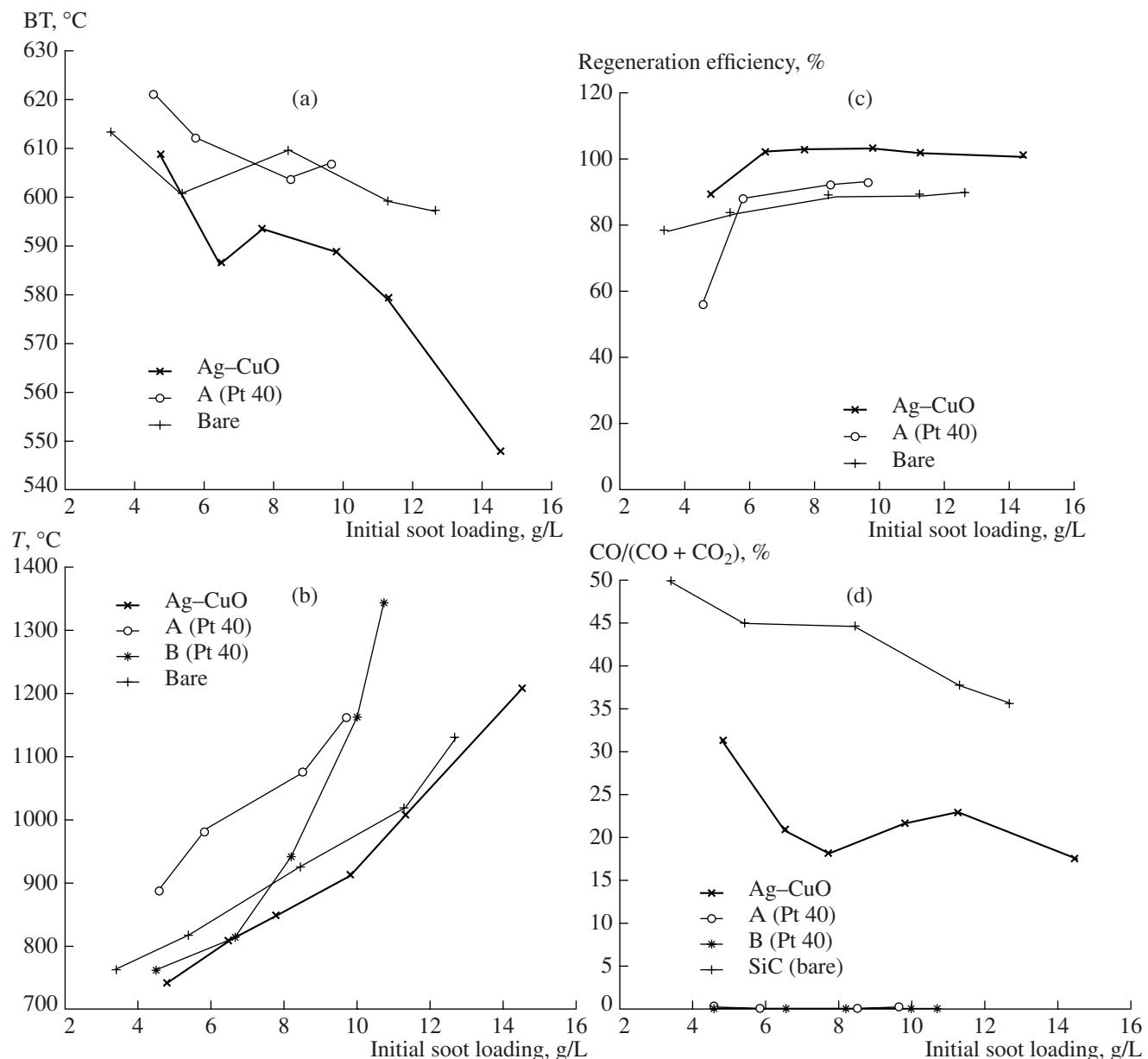


**Fig. 3.** Comparison of in-house coated DPFs, commercial prototypes A, B, C, and Blanc uncoated SiC filter on their performance in pressure drop balance temperature (BT, soot ignition temperature (a, c)) and soot regeneration efficiency (b, d) at different mass soot loadings, g/L DPF. Drop-to-idle regenerations of DPFs by periodical regeneration with oxygen at 600°C; DTIR: 1600 rpm/80 Nm. Sulfur level 50 ppm in fuel. Fuel post-injection was used to reach pre-DPFs  $T = 600^\circ\text{C}$  with the following idling to 900 rpm/0 Nm. Inhouse prepared DPFs no. 55-59 with PGM loadings 5–15 g/ft<sup>3</sup> in combination with  $\text{La}_2\text{CuO}_4$  and PGM-free Ag– $\text{La}_2\text{CuO}_4$  vs. commercial prototype DPFs A, B, and C having Pt loading 50–150 g/ft<sup>3</sup> and uncoated DPF.

soot in comparison with the active component spread on high-surface area refractory material like alumina. The monolayer of the active component can be obtained in this case at significantly lower catalyst loading relative to loading of preliminary washcoated material. As an example, the filter coated with only 0.5 wt % Ag and 2 wt % CuO provided a good performance in DPF regeneration. In addition, the zoning approach was used further to save silver; we used silver coating only for the entry of inlet channels to provide better soot ignition initiation. In general, the method of preparation was very simple with impregnation of the filter using a solution of copper nitrate and silver nitrate

for the 2"–2.5" of inlet channels and a solution of copper nitrate for the rest of the filter with the following drying and calcinations.

The Ag–CuO catalyst prepared based on the above findings [6] had an excellent performance, displaying a lower initiation temperature of soot oxidation, especially remarkable at high soot loadings, as presented in Fig. 4a. We also observed lower peak temperatures, even lower than that for the uncoated filter, allowing 3–3.5 g/L additional soot loading in comparison with Pt-comprising commercial DPFs, as can be seen in Fig. 4b. Regeneration efficiency was close to 100%, as is shown in Fig. 4c and higher relative to uncoated and reference



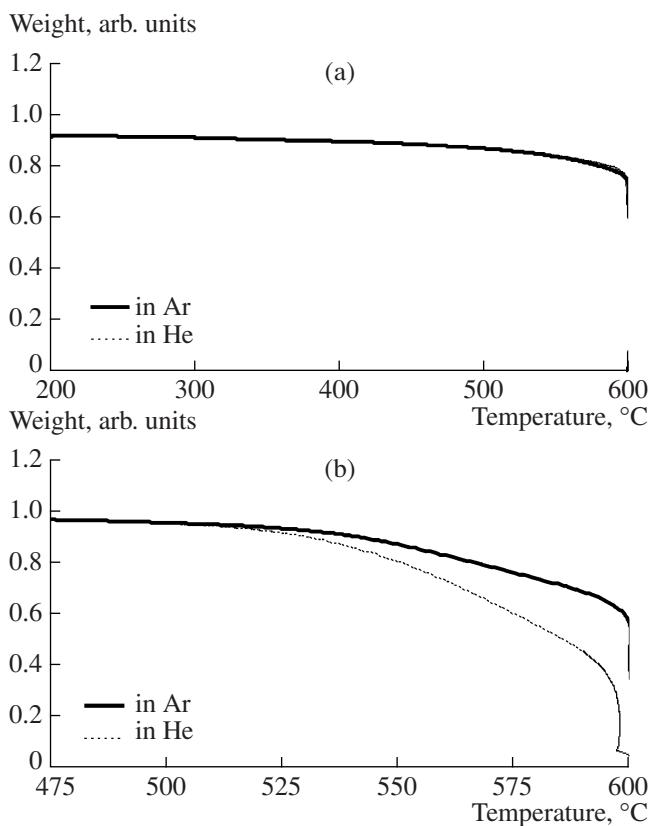
**Fig. 4.** Comparison of different DPFs technologies (Ag-CuO in-house made DPF, commercial prototypes A and B with 40 g/ft<sup>3</sup> Pt on their performance in pressure drop balance temperature (BT, soot ignition temperature, (a); maximal peak temperature (b) regeneration efficiency measured by  $\Delta P$  recovery (c) and selectivity of CO formation (d) during soot regenerations at different mass soot loadings, g/L DPF. Drop-to-idle regenerations (DTIRs) by periodical regeneration with oxygen at 600°C; DTIR 1600 rpm/80 Nm, Sulfur 50 ppm in fuel, fuel postinjection to reach pre-DPFs  $T = 600^\circ\text{C}$  with the following idling to 900 rpm/0 Nm.

Pt-containing DPFs. The catalyst was not able to oxidize CO to CO<sub>2</sub> completely, as can be seen in Fig. 4d in contrast to Pt-containing reference DPFs. Nevertheless, the amount of CO was near twice lower compared to the uncoated filter (see Fig. 4d), while peak temperatures were lower than for the uncoated filter despite the higher CO oxidation rate, as presented in Fig. 4b.

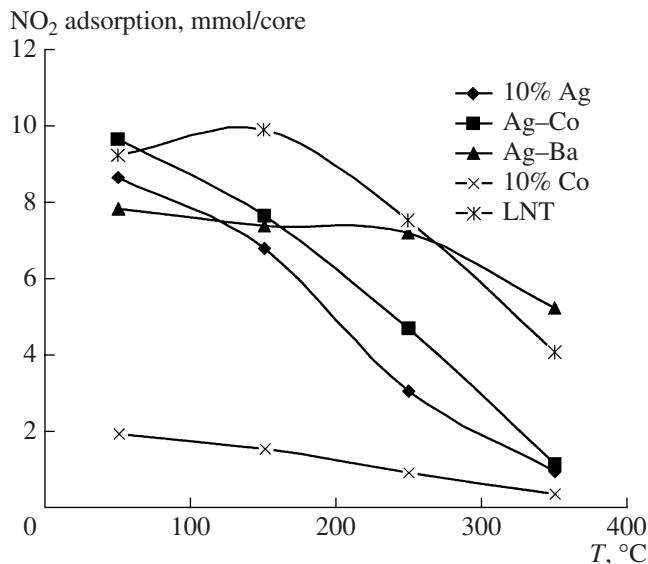
Gas-phase soot oxidation includes the following steps.



These features cause the basic features of soot oxidation by oxygen, namely very difficult initiation and high heat release, especially due to CO oxidation to CO<sub>2</sub>, where heat release is 2.7 times higher than for soot oxidation to CO. Despite the higher CO<sub>2</sub> release, the Ag-CuO catalyst allows lower peak temperatures compared to the uncoated filter for two basic reasons.



**Fig. 5.** TGA study of the effect of He or Ar as inert gas on soot oxidation on the Ag–CuO catalyst (a) and uncoated SiC (b). Experimental conditions: 40 mg of soot FW2, 240 mg of 1 wt % Ag–4 wt % CuO/SiC or 240 mg of uncoated SiC, 8% O<sub>2</sub> in He or Ar; flow 200 ml/min, heating rate 10 K/min.



**Fig. 6.** Comparison of NO<sub>2</sub> adsorption capacity of Ag- and Co-based catalysts vs. commercial LNT catalyst (100 g/ft<sup>3</sup> Pt, 10 g/ft<sup>3</sup> Rh, Ba–Ce as NO<sub>x</sub> storage material) at different temperatures. Reaction mixture 750 ppm NO<sub>2</sub>, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, 10% O<sub>2</sub>, balance N<sub>2</sub>, SV = 10 000 h<sup>-1</sup>, core samples 1" D × 1.5" L.

First, it initiates the soot oxidation at lower temperatures and earlier than the uncoated filter and, accordingly, heat is released for a longer time and more uniformly. Second, the thermal mass for Ag–CuO DPF was slightly higher, near 30 g of additional weight after the coating, though the contribution from higher thermal mass is small.

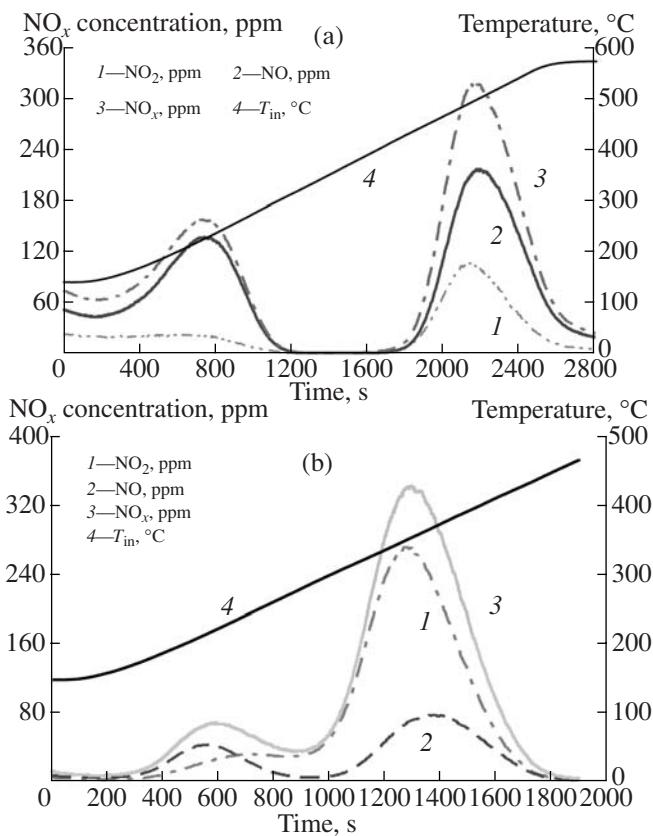
The additional advantage of this catalyst is that the impregnation from solution does not increase the resistance to flow and the Ag–CuO DPF had practically the same pressure drop for the clean filter, 27 mbar vs. 26 mbar for the uncoated filter. Meanwhile, commercial prototypes were prepared using the slurries, containing alumina, which partly block the channels and increase the pressure drop. As a result, these reference prototypes had 20–25% higher pressure drop for a clean filter that leads to a higher fuel penalty during the driving.

Generally, in comparison with Pt-containing catalysts, the Ag–CuO catalyst presented a quite different behavior during regeneration, being active in soot oxidation but not in the secondary reaction of CO oxidation.

Within the TGA study, we observed also an interesting effect upon replacing helium inert gas by argon, as shown in Fig. 5. The rate of soot oxidation with the Ag/CuO catalyst was significantly lower using Ar than in He (Fig. 5b), while for the mixture of soot with uncoated SiC powder the rate of soot oxidation was practically the same in the presence of Ar or He, as shown in Fig. 5a. As an example, 90% of soot was oxidized in the presence of the 1 wt % Ag–4 wt % CuO catalyst in 3 min using He and only after 13 min using Ar instead of He during steady-state soot oxidation at 600°C. It took near 60 min for 90% soot oxidation using uncoated SiC powder at 600°C. To explain such an effect, we proposed that this catalyst can release some active oxygen species locally, most probably atomic oxygen from the matrix into the gas phase, which can oxidize soot. In this case the diffusion of such oxygen forms is more complicated in Ar than in He; considering the distance between the catalyst and soot for “loose” contact. For example, the coefficient of binary diffusion D<sub>12</sub> is 2.996 cm<sup>2</sup>/s for the O<sub>2</sub>–He mixture and only 0.793 cm<sup>2</sup>/s for O<sub>2</sub>–Ar mixture [7]. For the gas-phase soot oxidation, atomic oxygen is generated in the gas-phase everywhere, including the near-surface region and can react with soot. We cannot exclude other explanations, however, and this phenomenon requires more detailed study.

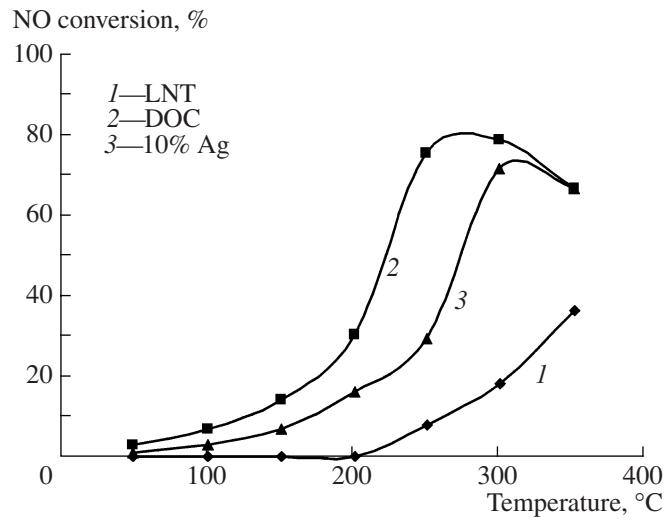
### 3.3. NO<sub>x</sub> Adsorption and Reduction Properties of Ag- and Co-Based Catalysts

Ag and Co-based catalysts were also tested in reactions of NO<sub>x</sub> accumulation, NO oxidation, SCR with H<sub>2</sub>, CO, and HC to evaluate them as possible candidates for lean NO<sub>x</sub> trap catalysts (LNT) and to understand the reason for their activity in soot oxidation with NO<sub>2</sub> assistance. A commercially available Pt–Rh LNT cata-

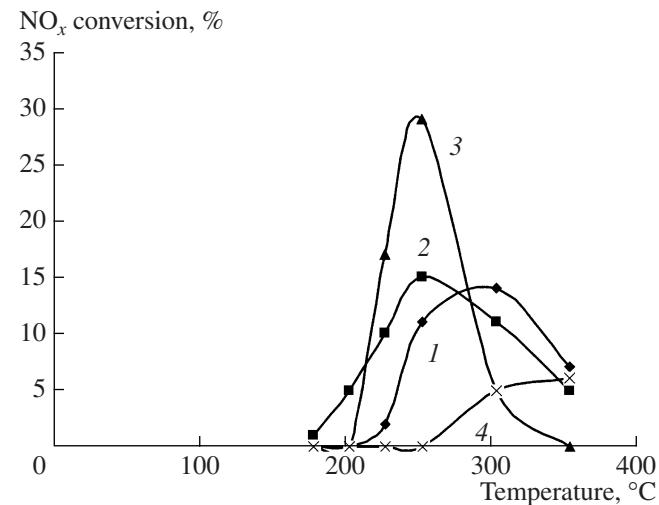


**Fig. 7.** Thermal desorption of  $\text{NO}_x$  species from 10 wt %  $\text{Ag}/\text{Al}_2\text{O}_3$ /cordierite after NO adsorption at  $150^\circ\text{C}$  (b) and commercial LNT (100 g/ $\text{ft}^3$  Pt, 10 g/ $\text{ft}^3$  Rh, Ba–Ce as  $\text{NO}_x$  storage material) (a) after treating samples in the gas mixture containing 750 ppm NO, 5%  $\text{CO}_2$ , 5%  $\text{H}_2\text{O}$ , 10%  $\text{O}_2$  in  $\text{N}_2$ ,  $\text{SV} = 10000 \text{ h}^{-1}$  until steady  $\text{NO}_x$  concentrations downstream from the reactor. Desorption was performed in the same mixture without NO with temperature ramp of 10 K/min; core samples 1" D  $\times$  1.5" L.

lyst containing barium as a basic component was used for comparison purposes, Pt-containing, commercial DOC too. Co-based catalysts showed quite low  $\text{NO}_x$  adsorption capacity for  $\text{NO}_2$  adsorption, as shown in Fig. 6. Except for high temperatures, Ag-based catalysts revealed quite good  $\text{NO}_x$  storage properties (high  $\text{NO}_x$  storage capacity) comparable to that of commercial LNT, as one can see in the same figure. For good  $\text{NO}_x$  storage properties, silver loading should be high, preferably 5–10 wt % of alumina-washcoated cordierite weight. The addition of barium can significantly increase the  $\text{NO}_x$  storage capacity of the silver catalyst at high temperatures, but we further found that barium unfortunately strongly suppress NO oxidation to  $\text{NO}_2$  on silver, so the catalyst cannot effectively store  $\text{NO}_x$  species when using NO instead of  $\text{NO}_2$ . We found a big difference between standard Pt–Rh–Ba–Ce LNT and silver-based formulations during thermo-programmed desorption after adsorption at different temperatures, as presented in Fig. 7. For LNT, NO was the main product



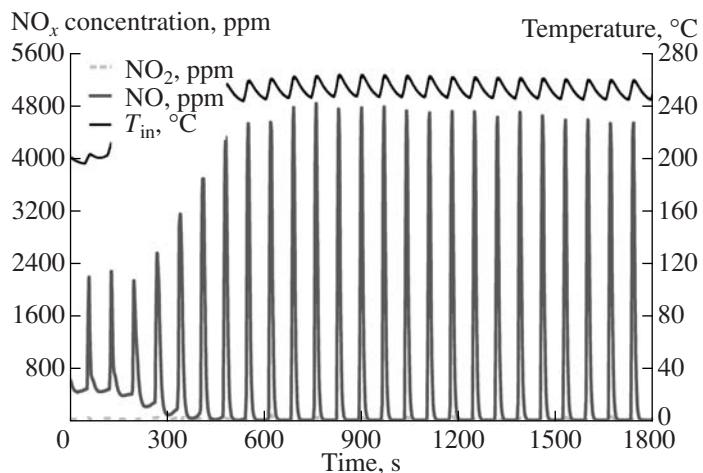
**Fig. 8.** Comparison of NO to  $\text{NO}_2$  oxidation properties of 10 wt %  $\text{Ag}/\text{Al}_2\text{O}_3$ /cordierite and reference commercial LNT (100 g/ $\text{ft}^3$  Pt, 10 g/ $\text{ft}^3$  Rh, Ba–Ce  $\text{NO}_x$ ) and diesel oxidation catalyst (DOC), 90 g/ $\text{ft}^3$  Pt. Reaction mixture 750 ppm NO, 5%  $\text{CO}_2$ , 5%  $\text{H}_2\text{O}$ , 10%  $\text{O}_2$  in  $\text{N}_2$ ,  $\text{SV} = 5000 \text{ h}^{-1}$ , core samples 1" D  $\times$  1.5" L.



**Fig. 9.** Lean de $\text{NO}_x$  activity of 10 wt %  $\text{Ag}/\text{Al}_2\text{O}_3$ /cordierite. Reaction mixture: 200 ppm NO, 5.5%  $\text{CO}_2$ , 5%  $\text{H}_2\text{O}$ , 10%  $\text{O}_2$ ,  $\text{N}_2$ —balance. Reductant: (1) 100 ppm  $\text{C}_3\text{H}_8$  + 700 ppm  $\text{C}_3\text{H}_6$  or (2) 2500 ppm CO or (3) 2500 ppm  $\text{H}_2$  or (4) 50 ppm  $\text{C}_3\text{H}_8$  + 350 ppm  $\text{C}_3\text{H}_6$  + 1250 ppm CO;  $\text{SV} = 10000 \text{ h}^{-1}$ , core samples 1" D  $\times$  1.5" L.

with NO release in two temperature regions, as pictured in Fig. 7a; while  $\text{NO}_2$  was the main product for TPD on the Ag-based catalyst. This adsorption–desorption study revealed two good features of the silver catalyst. It can store  $\text{NO}_x$  even at low temperatures and can release it as  $\text{NO}_2$  in the temperature region of 300–400°C, which is the most favorable for soot oxidation by  $\text{NO}_2$ .

Such systems can accumulate  $\text{NO}_x$  even at temperatures as low as 50°C [8]. For NO oxidation to  $\text{NO}_2$  on Ag-based catalysts, we observed good NO oxidation



**Fig. 10.**  $\text{NO}_x$  reduction under alternate lean–rich conditions at 250°C on 10 wt % Ag/Al<sub>2</sub>O<sub>3</sub>/cordierite. Lean conditions: 750 ppm NO, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, 10% O<sub>2</sub>,  $t = 60$  s. Rich conditions: 0.33% C<sub>3</sub>H<sub>6</sub>, 2.0% CO, 5% CO<sub>2</sub>, 5% H<sub>2</sub>O, 0.5% O<sub>2</sub>;  $t = 10$  s;  $T = 250^\circ\text{C}$ ; SV = 10000 h<sup>-1</sup>, core samples 1" D × 1.5" L.

activity, intermediate between the activity of LNT and DOC. It is remarkable that the Ag-catalyst was more active than the commercial costly LNT. The data are presented in Fig. 8. Pt–Rh based LNT for good  $\text{NO}_x$  storage always needs an oxide with strong basic properties, such as Ba, which can store  $\text{NO}_x$  species on its basic centers. In contrast, the Ag catalyst can both oxidize NO and store  $\text{NO}_x$  and does not need any basic oxide to store  $\text{NO}_x$ .

Unfortunately, the reducing properties of Ag-based catalyst were not so promising. For lean de $\text{NO}_x$  study under typical Diesel conditions, we found only moderate  $\text{NO}_x$  reduction efficiency (from 5 to 30% depending on conditions), as shown in Fig. 9. Low level of  $\text{NO}_x$  reduction was found for the mixture of CO and hydrocarbons, which is typical for Diesel conditions. However, the activity of LNT and DOC under the same lean de $\text{NO}_x$  conditions was also not impressive with up to 60–70%  $\text{NO}_x$  reduction within narrow temperature range.

The study of Ag-based catalyst under lean/rich cycling, representing typical mode for LNT application, was very disappointing. As can be seen in Fig. 10, Ag catalyst can effectively store  $\text{NO}_x$  under lean conditions, but releases practically all stored  $\text{NO}_x$  without reduction during rich pulses, thus leading to sharp peaks of NO up to 5000 ppm.  $\text{NO}_x$  conversion was only near 5%, while for commercial LNT more than 90% NO reduction was observed under the same conditions. We can conclude from these results that silver-based catalyst cannot provide significant  $\text{NO}_x$  reduction under Diesel conditions.

Based on the results obtained, such Ag-containing aftertreatment catalysts are the most promising for retrofit automotive applications to provide some moderate passive particulate matter (soot) and  $\text{NO}_x$  reduction. The Ag–CuO catalyst is very promising as a PGM-free

catalyst for high-temperature periodical soot oxidation with air on diesel passenger cars.

#### 4. CONCLUSIONS

- Against Pt-containing commercial prototypes, PGM-free Ag- and Co-based catalysts revealed comparable or better low-temperature  $\text{NO}_2$ -assisted soot regeneration activity, and the Ag–CuO catalyst had better performance for high-temperature periodical regenerations.

- Ag-based catalysts have shown good NO oxidation and  $\text{NO}_x$  accumulating properties with  $\text{NO}_2$  as the main product released during desorption, but it cannot effectively reduce the stored  $\text{NO}_x$  species.

- Ag-based catalysts can be recommended for retrofit applications to reduce passively PM and  $\text{NO}_x$  and high-temperature periodical regenerations for diesel passenger vehicles.

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