Development of silver-based catalytic materials for simultaneous removal of soot and NOx,

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Introduction
The new stringent regulation limits (EURO6) on the nitrogen oxides (NOx) and soot emissions are forcing to develop innovative catalytic systems that combine denitrification catalysts (such as NOx adsorption/reduction catalysts, LNT) with catalytic filters, according to the DPNR concept, recently developed by the Toyota group.

In LNT technology the NOx is reduced in two steps over a solid acid and noble metal/OSC material (where OSC indicates the oxygen storage capacity of the material). LNT catalysts work under cyclic conditions alternating a lean phase during which NOx in the exhausts are stored as nitrates/nitrates with a short rich phase, during which the stored NOx are reduced to nitrogen. During these cycles, soot removal occurs as well [1]. Recently, the combustion of soot was shown to be promoted by the presence of silver [2] and in the present investigation a series of metal oxide supports (CeO2, ZrO2, Al2O3) have been promoted with silver and alkaline metals (Ba or Sr) and the activity for the simultaneous removal of soot and NOx has been investigated.

Materials and Methods
The Ag(5%/wt)/Ba(10%/wt)/MxOy and Ag(5%/wt)/Sr(10%/wt)/MxOy (MxOy = CeO2, ZrO2, Al2O3) catalysts used in this study were prepared by incipient wetness impregnation with aqueous solutions of silver nitrate, barium acetate or strontium nitrate.

They were dried at 373 K overnight and calcined in air at 773 K for 3 h. All samples were characterized by XRD, TGA and BET; soot oxidation was carried out by running temperature programmed oxidation experiments (TPO) in different atmospheres (10%O2/N2 and 10%O2/500ppm NO/N2) under controlled conditions using a model soot (Printex-U, Degussa AG). Catalyst/soot mixtures in loose contact mode have been used for these preliminary tests. LNT activity was investigated under lean-rich conditions by alternating rectangular step feeds of NO (1000 ppm in He + 3%O2 v/v) with feeds of H2 (4000 ppm in He) under isothermal conditions at 350°C. These experiments have been performed both in the absence and in the presence of soot, the latter using a catalyst/soot ratio 9 to 1 by weight.

Results and Discussion
X-ray diffraction profiles show for each catalyst the formation of metallic silver and barium (or strontium) carbonate. Table 1 summarizes B.E.T. surface areas and catalytic activity for soot oxidation. As appears from these data, the presence of Ba, as storage component instead of Sr, decreases the onset temperature of the TPO both in the presence of only O2 and NO+O2; moreover, the lower temperature for the soot oxidation is observed when NO is co-feed to O2.

Table 1. B.E.T. measurements and catalytic activity results for soot oxidation

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>B.E.T. m²/g</th>
<th>Tp (O2) °C</th>
<th>Tp (O2/NO) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba/Ag/CeO₂</td>
<td>31</td>
<td>547</td>
<td>471</td>
</tr>
<tr>
<td>Ba/Ag/ZrO₂</td>
<td>38</td>
<td>528</td>
<td>465</td>
</tr>
<tr>
<td>Ba/Ag/Al₂O₃</td>
<td>144</td>
<td>503</td>
<td>480</td>
</tr>
</tbody>
</table>

In Figure 1 is reported a typical lean-rich cycle carried out over Ba/Ag/Al₂O₃ at 350°C in the absence of soot.

Figure 1. Lean (A) and rich phase (B) @ 350°C over Ba/Ag/Al₂O₃.

As a typical LNT catalyst, this system shows a good NOx breakthrough and an appreciable NO/NO2 oxidation, indicating a significant NOx storage capacity (Fig.1A). On the other hand, the subsequent rich phase results poorly selective to nitrogen showing a higher production of NO in the correspondence of the H2 admission (Fig.1B). When soot is mixed with the catalyst, soot combustion is observed during the lean phase. However, the NO/NO2 oxidation and the NOx breakthrough decrease, in line with the detrimental effect of soot on the storage capacity of LNT. Comparing the behavior of the prepared catalysts, the Ba-based systems show higher NOx breakthrough and higher NO/NO2 oxidation; also, the nitrogen selectivity increases even if results lower than the traditional LNT Pt-based catalysts.

Significance
Catalytic systems different from PMG-based LNT catalysts have been prepared, which are relevant for the development of improved NOx abatement systems.

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References