

Development of silver-based catalytic materials for simultaneous removal of soot and NO_x.

E. Aneggi¹, L. Castoldi², R. Matarrese², A. Trovarelli^{1*}, L. Lietti²

¹Università di Udine, DCFA, via Cotonificio 108, 33100 Udine, Italy

²Politecnico di Milano, Energy Department, p.za Leonardo da Vinci 32, 20133 Milano Italy

*corresponding author: trovarelli@uniud.it

Introduction

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

In LNT technology the NO_x 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 NO_x in the exhausts are stored as nitrites/nitrates with a short rich phase, during which the stored NO_x 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 NO_x 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

	B.E.T, m ² /g	Tp (O ₂) °C	Tp (O ₂ /NO) °C		B.E.T, m ² /g	Tp (O ₂) °C	Tp (O ₂ /NO) °C
Ba/Ag/CeO ₂	31	547	471	Sr/Ag/CeO ₂	20	550	472
Ba/Ag/ZrO ₂	38	528	465	Sr/Ag/ZrO ₂	31	550	470
Ba/Ag/Al ₂ O ₃	144	503	480	Sr/Ag/Al ₂ O ₃	145	587	515

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

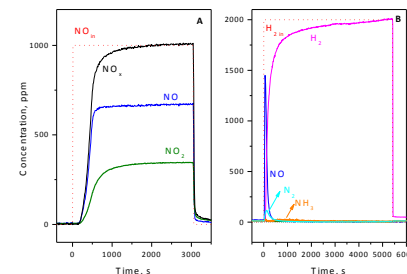


Figure 1. Lean (A) and rich phase (B) @ 350°C over Ba/Ag/Al₂O₃.

As a typical LNT catalyst, this system shows a good NO_x breakthrough and an appreciable NO/NO₂ oxidation, indicating a significant NO_x 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 NO_x 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 NO_x 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 NO_x abatement systems.

Acknowledgements

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References

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