

Study of the interaction between Desoot and DeNO_x activity over Ba- and K-based LNT catalysts

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Introduction

Regarding automotive emissions, the new stringent regulation limits (EURO6) are forcing to develop innovative catalytic systems that combine denitrification catalysts with catalytic filters. The DPNR (Diesel Particulate NO_x Reduction) system, which involves the use of LNT catalysts, is the first commercialized example of such a technology [1]. In previous works of our group the capability of model DPNR catalysts (e.g. Pt-Ba/Al₂O₃ and Pt-K/Al₂O₃) to simultaneously remove soot and NO_x has been investigated [2,3]. It has been found that an interplay exists between the NO_x storage-reduction function of the catalyst and the soot oxidation. Accordingly aim of this work is to provide new insights on the interaction between soot and the stored NO_x species; for this purpose temperature programmed methods were used.

Experimental

Home made PtBa/Al₂O₃ (1/20/100 w/w) and PtK/Al₂O₃ (1/5.4/100 w/w) catalysts were prepared by impregnation of γ -alumina. TPD and TPO experiments were performed in a flow micro-reactor system, consisting of a quartz tube (7 mm i.d.), equipped with a mass spectrometer, a micro GC and an UV analyzer for the on-line analysis of the outlet gases. NO_x have been stored onto the catalytic surface at 350°C with NO/O₂ or NO₂ in the absence of soot. Then the samples were cooled in He and finally heated (10 °C/min) up to 500°C in the absence of soot and after mixing with soot. Also binary samples (e.g. Ba/Al₂O₃ and K/Al₂O₃) were prepared and tested in order to investigate the specific role of Pt and of the NO_x storage metal (i.e. Ba or K) in the DeNO_x-Desoot activity.

Results/Discussion

The results of the TPD runs performed over Pt-Ba/Al₂O₃ catalyst in the absence and in the presence of soot are shown in Figure 1A and 1B, respectively.

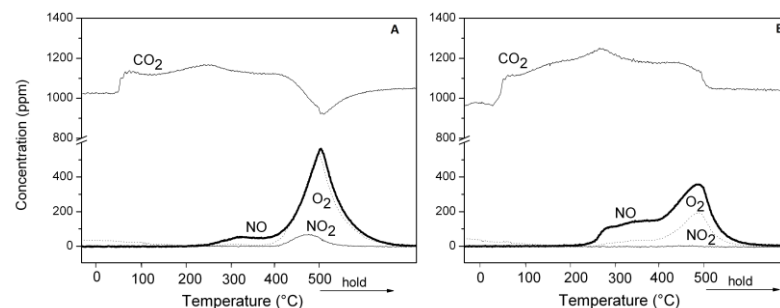


Figure 1. TPD experiments: runs after NO_x adsorption at 350°C over Pt-Ba/Al₂O₃ catalyst (A); Pt-Ba/Al₂O₃ catalyst-soot mixture (B).

In the case of the soot-free catalyst (figure 1A) most of the nitrate decomposition is observed above 350 °C (the adsorption temperature) with the evolution of NO and O₂ and minor amounts of NO₂. In correspondence of NO_x and oxygen evolution an uptake of CO₂ is observed due to the formation of barium carbonates. The NO_x decomposition process is not complete at temperatures as high as 500 °C. The presence of soot leads to significant changes in the TPD spectra (Figure 1B). In this case a significant release of NO and O₂ is observed in the temperature range 260-350 °C. The decomposition of nitrates is then completed above 350 °C, with a NO peak maximum near 485 °C. Of note, the distribution of desorbed products is different in this case: no NO₂ along with minor amounts of O₂ are detected at the reactor outlet due to their involvement in the soot oxidation. As a matter of fact, no CO₂ uptake is observed. Notably, below 350°C (i.e. before the onset of nitrate thermal decomposition) the concentration of the evolved products obeys the stoichiometry of nitrate reduction by soot:



This suggests the direct interaction between nitrate ad-species and soot which can be explained on the basis of the surface mobility of the adsorbed nitrates. The driving force for this process may be the presence of carbon reducible sites, in analogy with the pathway proposed for nitrate reduction during lean/rich operation of LNT catalysts.

Very similar results have been obtained over the K-based LNT catalysts, but a more relevant interaction between soot and the adsorbed NO_x has been pointed out, possibly related to the higher mobility of the adsorbed NO_x species present on the K-based samples.

References.

1. K. Nakatani, S. Hirota, S. Takeshima, K. Itoh, T. Tanaka, K. Dohmae, *SAE paper* N. 01-0957. (2002)
2. R. Matarrese, L. Castoldi, L. Lietti, P. Forzatti, *Topics in Catalysis* **5**,2041 (2009)