

Combined NO_x and soot abatement over Pt-Ba/γ-Al₂O₃ DPNR model catalyst

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Introduction

Due to progressive increase of the Diesel engines' market and more stringent legislative regulations on vehicle emissions, in recent years considerable efforts have been devoted to the study of abatement technologies able to reduce both soot and NO_x emissions. In the late '90 Toyota has developed a new after-treatment technology called Diesel Particulate-NO_x Reduction (DPNR), consisting of a ceramic filter coated with a catalytic layer of NSR (NO_x Storage-Reduction) catalyst. The system utilizes cyclic operations by switching between fuel-lean and fuel-rich conditions. The aim of the present study is to analyze the effects of the presence of soot on the behaviour of the DPNR catalysts in terms of NO_x storage/reduction efficiency and to provide new insights on the role of stored NO_x in soot combustion.

Experimental part

Homemade Pt-Ba/Al₂O₃ (1/20/100 w/w) catalyst has been prepared by the wetness impregnation from aqueous solutions of dinitrodiammine platinum and barium acetate. In order to analyze the effect of the presence of soot on catalyst activity, catalyst/model soot (Printex U) mixture with 9/1 (w/w) ratio has been employed. The NO_x storage-reduction activity and the effect of soot on the thermal stability/reactivity of the adsorbed nitrates have been investigated by several techniques, including lean-rich cycles (rectangular step feeds of NO, 1000 ppm, in He+3% v/v O₂ alternated with 4000 ppm of H₂ in He), TPD and TPO experiments (heating rate 10 °C/min in He or in O₂ (3%) from 250°C up to 500°C), in the presence and in the absence of soot.

Results and discussion

The results obtained during the lean NO_x adsorption over the Pt-Ba/Al₂O₃-soot mixture showed that the presence of soot decreases the NO_x storage capacity of the soot-free catalyst^[1]. In presence of soot the amount of NO_x stored at saturation is near 0.58 and 0.41 mmol/g_{cat} without soot (reduced to 0.47 and 0.28 mmol/g_{cat} upon NO shutoff, respectively). During the lean-rich cycles, soot oxidation also takes place, as pointed out by CO₂ evolution. In particular during the lean phase the soot combustion is observed only upon NO admission, and it is almost negligible in the presence of O₂ only. To better analyse these aspects, TPD and TPO experiments of adsorbed NO_x have been carried out with and without soot. As pointed out by TPD run in absence of soot (Fig.1.A), desorption peaks were observed at 350°C, the adsorption temperature. The nitrate decomposition gives the formation of NO₂ at low temperature and then NO+O₂; a decrease of the CO₂ signal is also observed due to the re-adsorption of CO₂ on Ba forming BaCO₃ upon decomposition of Ba nitrates. In presence of soot (Fig.1.B), the decomposition onset of the stored NO_x is observed

about at the same temperature, but the distribution of desorbed products is different. Only NO is observed as decomposition product; in fact, NO₂ and O₂ from the nitrates decomposition are readily consumed in the soot combustion as shown by the increase of net CO₂ concentration trace. However, a direct participation of the stored NO_x in the soot oxidation cannot be excluded. It is worth noticing that with soot, the amounts of desorbed species is lower than that calculated without soot as consequence of the minor amounts of NO_x adsorbed in the presence of soot. The quantitative balance of the amounts of stored and desorbed species close within 5%. Moreover, the nitrates decomposition is concluded at lower temperature, indicating that soot favours the decomposition of NO_x adsorbed species^[2]. These results are confirmed with those obtained in TPO experiment. Considering TPO run in absence of soot (Fig.2.A), it appears that the products distribution is similar to that observed in TPD experiment, with NO₂ and NO evolution above 350°C. At the end of the heating ramp (500°C), the nitrate decomposition process was not complete, pointing to a role of O₂ on NO_x decomposition. In correspondence of the NO_x desorption peak, a decrease in CO₂ concentration trace is observed, due to carbonates formation. With soot (Fig.2.B), the nitrates decomposition occurs at slightly lower temperatures than in the absence of soot. As already reported in the TPD run, no NO₂ is detected at the reactor outlet due to its consumption in the soot oxidation. A significant CO₂ evolution is observed, along with O₂ consumption. At 500°C the decomposition of nitrates is already complete. The participation of the adsorbed NO_x in the soot oxidation has also been pointed out by TPO experiments with and without pre-adsorbed nitrates (not shown): oxidation of soot is greatly enhanced by the presence of adsorbed NO_x species as indicated by the larger amounts of CO₂ produced upon soot oxidation. In conclusion, the presence of soot decreases the NO_x storage and the stability of adsorbed species: this shows a complex interplay existing between soot and stored NO_x. The participation of stored NO_x in soot oxidation, by direct participation or upon the release of NO₂ and O₂ in the gas phase, has been also pointed out.

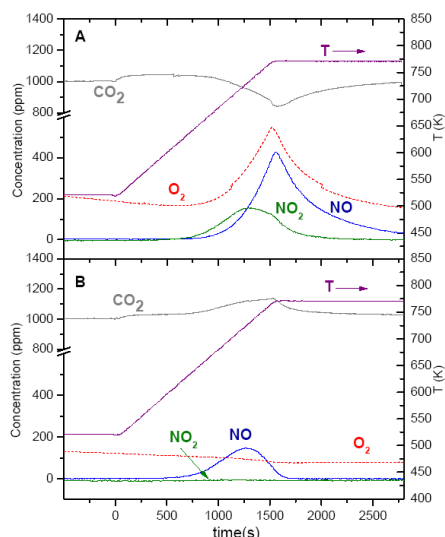


Fig.1. TPD run after NO_x adsorption at 350°C over (A) PtBa/Al₂O₃ catalyst; (B) PtBa/Al₂O₃ catalyst-soot mixture, obtained in presence of H₂O 1% and CO₂ 0.1%

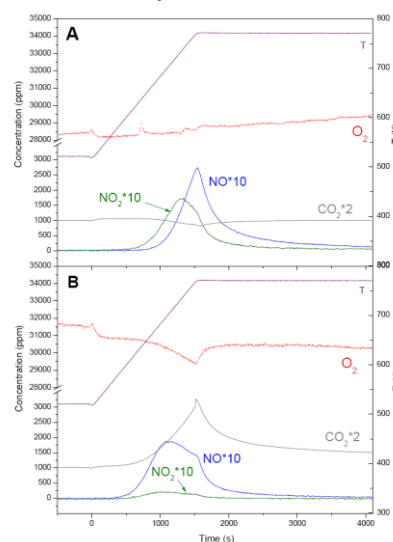


Fig.2. TPO run after NO_x adsorption at 350°C (in presence of H₂O 1% and CO₂ 0.1%) over A) PtBa/Al₂O₃ catalyst; B) PtBa/Al₂O₃ catalyst-soot mixture; CO₂ trace is reported with 1000 ppm offset.

[1] L. Castoldi, N. Artioli, R. Matarrese, L. Lietti, P. Forzatti, *Catal. Today* (2010), doi:10.1016/j.cattod.2010.03.022

[2] A.L. Kustov, M. Makkee, *Appl. Catal. B*, 88 (2009) 263