

## NO<sub>x</sub> and soot removal over Ba- and K-based Pt/Al<sub>2</sub>O<sub>3</sub> 4-ways catalysts

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### Introduction

The tightening of diesel emissions limits is nowadays driving research and development on control technologies for the reduction of harmful diesel exhaust emissions. The so-called 4 ways catalysts able to reduce NO<sub>x</sub> as well as CO, HC and particulate in the diesel exhaust emission are under development. Among these, the DPNR<sup>[1]</sup> (Diesel Particulate NO<sub>x</sub> Reduction) technique, which involves the use of a lean NO<sub>x</sub> trap catalyst (e.g. Pt-Ba/Al<sub>2</sub>O<sub>3</sub>) working under lean-rich cycling conditions, is the first commercialized example of such a technology<sup>[2,3]</sup>. Further improvement of the DPNR techniques are however needed in view of enhancing the system's efficiency to comply with future lower emission requirements. In a previous paper<sup>[3]</sup> we have considered the reactivity of model Pt-Ba/Al<sub>2</sub>O<sub>3</sub> and Pt-K/Al<sub>2</sub>O<sub>3</sub> catalyst samples in the simultaneous removal of NO<sub>x</sub> and soot. Under model "clean" conditions the selected catalyst samples are able to simultaneously remove soot and NO<sub>x</sub> when operating under cycling conditions, but the K-containing sample is by far more active in the soot combustion than the Ba-based catalyst.

In this work, to provide further insights on the reactivity of Pt-Ba/Al<sub>2</sub>O<sub>3</sub> and Pt-K/Al<sub>2</sub>O<sub>3</sub> DPNR catalysts, and on the interaction between the NO<sub>x</sub> reduction and the soot oxidation functions, the catalytic behaviour of the same Pt-Ba/Al<sub>2</sub>O<sub>3</sub> and Pt-K/Al<sub>2</sub>O<sub>3</sub> catalyst samples used in previous studies has been analyzed under different experimental conditions.

### Materials and Methods

The selected Pt-Ba/Al<sub>2</sub>O<sub>3</sub> (1/16/100 w/w) and Pt-K/Al<sub>2</sub>O<sub>3</sub> (1/5.4/100 w/w) model catalysts were mixed with the soot (Printex U from Degussa, catalyst/soot ratio ranging from 8/2 to 9.8/0.2 w/w) and tested in the simultaneous NO<sub>x</sub> storage-reduction and soot removal by the transient response method (TRM). Experiments were performed in a flow micro-reactor system by alternating rectangular step feeds of NO (250-1000 ppm) in He + 3% v/v O<sub>2</sub> (lean phase) and of hydrogen (2000 ppm) in He (rich phase), separated by a He purge in between. To analyze the role of CO<sub>2</sub> and water on the simultaneous NO<sub>x</sub> storage-reduction/soot oxidation capability of the catalysts experiments have been performed in the absence and in the presence of CO<sub>2</sub> (3000 ppm) and H<sub>2</sub>O (1%).

### Results and Discussion

The results obtained during a lean phase, in the presence of CO<sub>2</sub> and H<sub>2</sub>O, for the Pt-Ba/Al<sub>2</sub>O<sub>3</sub> and Pt-K/Al<sub>2</sub>O<sub>3</sub>-soot mixture are shown in Fig. 1A and 1B, respectively. In both cases the data showed a NO<sub>x</sub> dead time, pointing out both systems are able to store nitrogen oxides, even in the presence of soot. CO<sub>2</sub> is also evolved during the lean phase, in part originating from NO<sub>x</sub> adsorption (which leads to Ba carbonate decomposition), and in part from soot oxidation. The net amount of CO<sub>2</sub>, which is due to soot oxidation, is shown in figure 1 as dotted line and is estimated by subtracting from the CO<sub>2</sub> profile the amount of CO<sub>2</sub>

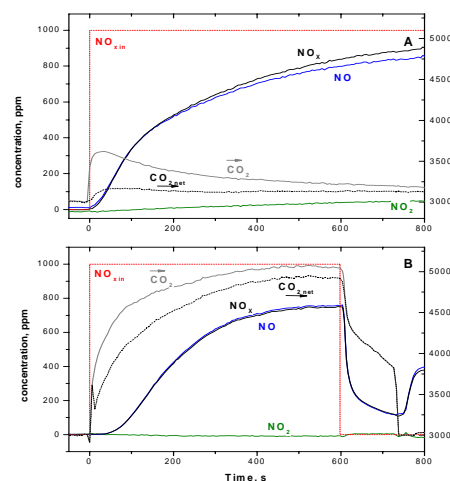


Fig.1 – Results of NO (1000ppm)/O<sub>2</sub>(3%) adsorption over Pt-Ba/Al<sub>2</sub>O<sub>3</sub> + soot mixture (A) and Pt-K/Al<sub>2</sub>O<sub>3</sub> + soot mixture (B), in presence of CO<sub>2</sub> (3000 ppm) and H<sub>2</sub>O (1%) @ 350°C

released upon NO<sub>x</sub> adsorption. Upon NO admission, the CO<sub>2</sub> evolution indicates that the soot oxidation takes place during the storage of NO<sub>x</sub>. By comparing the net CO<sub>2</sub> concentration traces of Figures 1A and 1B (i.e. the CO<sub>2</sub> originating from soot oxidation) it appears that both the Pt-Ba/Al<sub>2</sub>O<sub>3</sub> and Pt-K/Al<sub>2</sub>O<sub>3</sub> catalysts are able to remove soot, but the Pt-K/Al<sub>2</sub>O<sub>3</sub> system clearly shows superior characteristics with respect to Pt-Ba/Al<sub>2</sub>O<sub>3</sub>. As a matter of fact, during a single 10 min storage cycle 1% of soot has been combusted in the case of the Ba-based system and 15 % in the case of Pt-K/Al<sub>2</sub>O<sub>3</sub>. The storage phase has also been investigated at different NO concentrations, in the range of 250-1000 ppm. The results pointed out that decreasing the inlet NO concentration the NO<sub>x</sub> breakthrough increases. Also the soot combustion decreased, but not linearly with the decrease of the NO concentration. This indicates that both gas phase NO<sub>x</sub> and stored NO<sub>x</sub>

may play a role on soot oxidation. Storage cycles were performed at different temperatures, in the range 250–350°C. The results indicate that the efficiency of both the NO<sub>x</sub> removal and soot oxidation increases on increasing the temperature. Finally, the results of lean-rich cycles performed with different catalyst/soot ratios show that at the highest investigated soot loadings (catalyst/soot ratio of 8:2 w/w) the NO<sub>x</sub> storage capacity is decreased. On the other hand the activity in the soot combustion apparently increases with increasing the soot loading.

### Significance

The interaction between soot oxidation and NO<sub>x</sub> storage capacity has been pointed out, which is helpful in understanding the catalytic behavior of DPNR systems and which is relevant for the selection of appropriate key-parameters.

### References

1. Koichiro, N., Hirota, S., Takeshima, S., Itoh, K., Tanaka, T., Dohmae, K. *SAE Technical Paper* (2002) N. 01-0957
2. Castoldi, L., Matarrese, R., Lietti, L., Forzatti, P. *Appl. Catal B: Environmental* 64, 25 (2006)
3. Matarrese, R., Castoldi, L., Lietti, L., Forzatti, P. *Top. Catal.* 42-43, 293 (2007)