Effect of Pd addition on the efficiency of a NO_x-trap catalyst: a FTIR *operando* study

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Introduction and Objectives

In the quest for more energetically and ecologically efficient exhaust control systems, a promising approach called Lean-NO_x-trap (LNT) was developed by Toyota in order to remove NO_x from lean burn engines vehicles [1]. The LNT process consists in a first NO oxidation over precious metals (Pt, Pd or Rh) followed by a subsequent trap onto alkaline or alkali earth compounds during rather long lean periods. When the saturation is reached, the catalyst is exposed to a short rich period, during which the storage medium regeneration proceeds through the reduction of the stored NO_x to nitrogen onto noble metals [2]. Due to their high price and incoming shortage, noble metals are the target of numerous studies, in order to limit their concentration and nature. While most of the works focused on Pt as the noble metal, a limited number of investigators also examined the efficiency of Pd, known to be a more active oxidation catalyst for short-chain hydrocarbons [3]. The aim of the present work is thus to study the effect of Pd addition over a commercial $Pt/Ba/CeO_2/Al_2O_3$ based catalyst, using a gas mixture simulating a real Diesel engine exhaust gas composition. A FTIR *Operando* study has allowed to further analyze the mechanisms occurring on the catalyst surface and to highlight the most critical points.

Results and Discussion

Two main catalysts were studied: a monometallic Pt (1.3 wt.%) and a bimetallic Pt-Pd (1.3 wt.%, mass ratio Pt/Pd = 27) both supported onto $Ba/CeO_2/Al_2O_3$. For comparison purpose, the reaction over the metal free support was also performed. A model gas composition which closely mimics a Diesel engine exhaust gas was used, including NO, O_2 and CO traces in the lean, decane, CO, H_2 and O_2 in the rich flows. Water and CO_2 were also added for realistic considerations. The nitration tests were carried out at different temperatures representative of typical engine conditions during vehicle operation.

The results relative to the quantification of NO oxidation into NO_2 and NO_x storing are presented in Figure 1 (left). At 573 K the highest NO_x storage capacity is observed for all samples and the Pt-Pd catalyst appears to be the most efficient storing system due to its highest NO oxidation capacity. Noble metals are indeed mainly involved in the oxidation of NO under lean conditions, but they can also be involved in other reactions, such as steam reforming or partial oxidation of hydrocarbons, Water Gas Shift and CO oxidation. Our results suggest that CO oxidation could be facilitated by Pd, while Pt would mainly

oxidize NO to NO_2. *Operando* FTIR enabled to analyze the evolution of adsorbed species upon nitration time on stream (Figure 1 centre). For the bare support, a negative band is observed at 1644 cm^{-1} than can be assigned to acrylates arising from decane decomposition. For monometallic Pt and bimetallic Pt-Pd this band is much less intense, indicating that the presence of noble metals favors the complete decane combustion during the preliminary material stabilization under rich flow. Furthermore, the spectra evolution evidences that carbonate species are substituted by nitrates, being the intensity of nitrate bands higher for the bimetallic Pt-Pd catalyst. This last result is consistent with both the higher NO oxidation capacity and NO_x storing capacity observed with this catalyst.

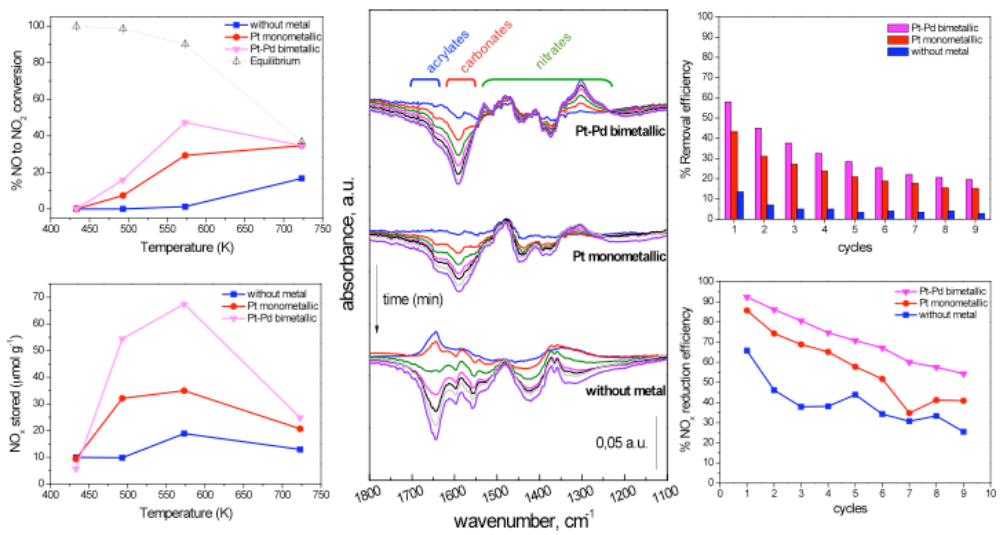

Figure 1. NO to NO_2 conversion (top left) and NO_x stored (bottom left) evolution with reaction temperature, difference surface spectra collected during nitration at 573 K (centre), removal efficiency (top right) and NO_x reduction efficiency (bottom left) during cycles for three samples.

Figure 1 (right) shows the results obtained during lean/rich cycles. Pd addition clearly improved both the removal efficiency and the NO_x reduction efficiency. A synergistic effect between Pt and Pd is thus evidenced for the LNT process. The progressive loss of efficiency observed upon increasing number of cycles is due to little NO_x accumulation, being unable the catalyst to fully recover its initial state under rich flow at 553 K.

Conclusions

The use of an *operando* IR/MS approach has allowed evidencing a synergistic effect existing between Pt and Pd to improve the NO to NO_2 oxidation and therefore the NO_x storage capacity in a LNT catalyst.

References

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