# APPRAISAL OF A DE-NOX SYSTEM BASED ON $H_2$ FOR LIGHT-DUTY DIESEL ENGINE VEHICLES

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*Summary*

The paper describes a novel after-treatment system based on hydrogen for de-NOx purposes for light duty diesel engines applications. Hydrogen is generated by an ATR, placed as a bypass of the close coupled DOC and DPF, and promotes NOx reduction in a specific catalytic converter in under-floor position. Tests on commercial reforming catalysts, and on $H_2$-SCR perovskite catalysts synthesized within our group, are presented. The best catalyst was $La_{0.7}Sr_{0.2}Ce_{0.1}Fe_{0.9}Pd_{0.1}O_3$, exhibiting a very low $T_{50}$ (150°C) compared to other systems. The associated fuel penalty is around 4% for a 60% NOx conversion, which requires further improvements under lean conditions.

*Keywords*

Environmental Reaction Engineering, Novel reactor technologies.

## Introduction

A combination of engine modifications and after-treatment technologies is suggested to achieve compliance with future legislative limits. Selective catalytic reduction (SCR) is about to be introduced for the reduction of nitrogen oxides in light-duty diesel vehicles. The prevalent technology available to control $NO_x$ emission is indeed the selective catalytic reduction (SCR) by $NH_3$ (Forzatti, 2001). As an alternative option, the use of CO and light hydrocarbons, already present in the vehicle exhaust or generated on purpose, has been extensively studied in the seek of alternative reducing agents. More recently, the use of hydrogen as a reductant has been explored, showing a good promise (Ferri et al., 1998; Costa et. al, 2002; Costa and Efstathiou, 2007). Hence, within the framework of a European research project (Top-Expert, 2006-2009), the Authors have started, with leading industrial companies, an investigation on the adoption of a small reformer on board for $H_2$ generation from directly injected diesel oil, to promote the $NO_x$ SCR by $H_2$.

## System Description

The following after-treatment system is based on the on-board generation of activated species, able to reduce $NO_x$ emissions from diesel engines. $H_2$ and CO are produced through an auto-thermal reforming (ATR) of post-injected fuel, placed as a by-pass of the close coupled DOC (Diesel Oxidation Catalyst) and DPF (Diesel Particulate Filter), as depicted in **Fig. 1**. The proper inlet composition to the reformer is achieved by the simultaneous control of the exhaust gas flow rate, split from the main flow by means

of a plug valve, and the required amount of vaporized diesel, fed to the reformer at the front of the reactor. In fact, an appropriate oxygen to carbon ratio has to be ensured into the reformer to enhance $H_2$ selectivity, and consequently for fuel penalty minimization. A spark ignition system is placed to eliminate light off issues, since the gaseous flow is in some cases below the minimum temperature to activate the reformer catalyst.
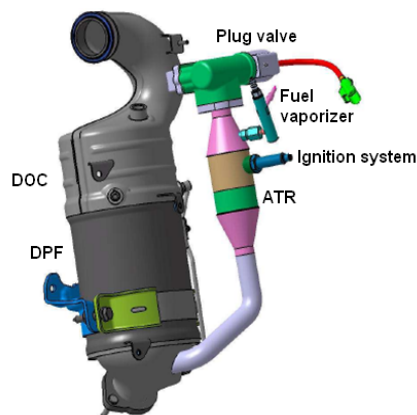


Fig. 1 Prototype of the system.

*Active species generation*

A study case focused on the emissions of a D-segment vehicle equipped with 2.0l-16 valves common rail diesel engine is here described. Some commercial catalysts were tested in order to investigate the performance of the ATR under such conditions. The purpose of the tests is to determine the optimal oxygen to carbon ratio to drive the

reforming reaction using a commercial catalyst. The tests enlighten the reformer performance at different oxygen to carbon ratios and space velocities.

The best operating conditions is at a GSHV of 20400 h$^{-1}$, and an oxygen to carbon ratio equal to 0.5. Other oxygen to carbon ratios performed worse either because there was not enough heat produced in the system ($O_2/C<0.4$) or excessive fuel underwent a total combustion and no more fuel was available for reforming ($O_2/C>0.6$). Conversely, at higher space velocities total/partial combustion dominates kinetically and despite the big amount of produced heat, steam reforming has a low reaction rate because of the short residence time. Instead, for low space velocities, the water gas shift reaction is shifted towards the production of $H_2O$ and $CO$ (endothermic reaction) because of the low $H_2O$ concentration in the system. At each engine operative condition, given an optimal oxygen to carbon ratio in the ATR, and a required $H_2$ yield for NOx reduction, fuel consumption can be evaluated, and the exhaust gases split to the ATR is sized accordingly.

*NO$_x$ reduction*

A series of perovskite-type catalysts ($LaFeO_3$, $La_{0.8}Sr_{0.2}FeO_3$, $Pd/La_{0.8}Sr_{0.2}FeO_3$, $La_{0.8}Sr_{0.2}Fe_{0.9}Pd_{0.1}O_3$, $La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$, $La_{0.7}Sr_{0.2}Ce_{0.1}Fe_{0.9}Pd_{0.1}O_3$, $Pd/La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$) were prepared by the solution combustion synthesis method (details in Civera et al., 2003) and fully characterized by XRD, BET, FESEM and TPD/R analyses. Two of them ($Pd/La_{0.8}Sr_{0.2}FeO_3$, $Pd/La_{0.7}Sr_{0.2}Ce_{0.1}FeO_3$) were prepared by deposition of the Pd nitrate precursor via incipient wetness impregnation onto the pre-formed perovskites. It has to be underlined that all the elements included in the catalyst formulations are compatible with the devised application, as they are widely employed in three-way catalysts (Pd, Ce, La) or not harmful at all (Fe). For the sake of brevity, the results of the catalytic activity tests are shown only for $La_{0.7}Sr_{0.2}Ce_{0.1}Fe_{0.9}Pd_{0.1}O_3$, which was selected as the best catalyst on the grounds of temperature programmed reduction (TPR) and desorption (TPD) tests on powders. The NO reduction towards $N_2$ operated by the catalyst was evaluated in a temperature programmed reaction apparatus (TPRe) in the absence and in the presence of oxygen. The catalyst was deposited over a cordierite substrate (diameter: 35 mm, length: 25 mm, cell density: 200 cpsi; from Céramiques Techniques Industrielles), coated with 5wt% γ-alumina, at a loading W/F equal to 0.02 $g_{cat}$·s·cm$^{-3}$ (20 wt%). In **Fig. 2-left** it appears that for a mixture of 1,000 ppmv of NO and 10,000 ppmv of $H_2$, without the presence of oxygen, the catalyst has a $T_{50}$ equal to 130 °C at 30000 h$^{-1}$, with a complete NO reduction at about 200 °C. In the presence of oxygen (5 vol%), at least a two folds higher hydrogen concentration was required to achieve approximately the same NO to $N_2$ reduction level obtained with the catalyst in the powder form (see **Fig. 2-right**).
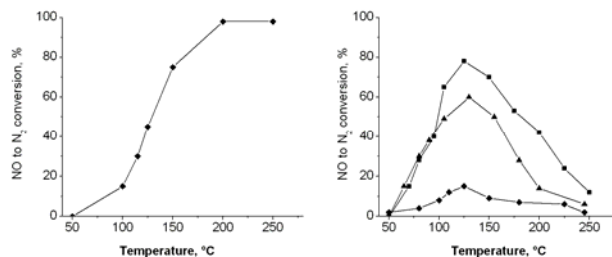


Fig. 2 GSHV = 30,000 h$^{-1}$. Left: 1,000 ppmv NO, 10,000 ppmv $H_2$ (♦), $N_2$ balance; Right: 100 ppmv NO, 1,000 (♦) – 2,000 (▲) – 4,000 (■) ppmv $H_2$, 5% $O_2$, $N_2$ balance.

## Conclusions

A novel system for $NO_x$ reduction through on-board hydrogen generation was described. The fuel consumption was evaluated by investigating the performance of several perovskite-type oxide catalysts, developed for the selective catalytic reduction of NO to $N_2$ promoted by hydrogen. The results are obtained for GHSV of practical interest and temperatures (130 °C - 150 °C) compatible with those of the exhaust line of a diesel passenger car. Studies are now in progress to improve the catalyst selectivity in the presence of oxygen, by maximizing $N_2$ production and lowering $N_2O$ and $NO_2$ ones, for fuel consumption minimization. Hence, at present the fuel penalty is around 4% for a $NO_x$ conversion to $N_2$ equal to 60%, which limits its possible direct application.

As compared to other catalysts of $H_2$-SCR found in the literature (Ferri et al., 1998; Costa et. al, 2002; Costa and Efstathiou, 2007), the $NO_x$ conversion is satisfactory since it is reached without the use of Pt, and with a low W/F factor (mass of catalyst over the flow rate).

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