

HC-SCR on Silver-Based Catalyst: From Synthetic Gas Bench to Real Use

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ABSTRACT

The challenge for decreasing the emissions of compression ignition engines now remains mainly on NO_x control. If the Lean NO_x Trap (LNT) and Selective Catalytic Reduction by Urea (Urea-SCR) are very efficient, their extra-cost and management are a major issue for the OEMs. In that context, the selective catalytic reduction by hydrocarbons (HC-SCR) appears to be an interesting alternative solution, with a more limited NO_x conversion efficiency but an easier packaging (diesel fuel as a reductant) and a limited price (reasonable coating cost / no PGM).

In the framework of the RedNO_x project, a prototype catalyst made of 2% silver on Alumina coated on cordierite was manufactured and tested on a synthetic gas bench. In parallel, an exhaust implementation study has been led to ensure the most suited conditions for injection. Thanks to SGB and simulation results, adapted engine tests have been designed and performed.

If the results on SGB are consistent with the literature with a maximum NO_x conversion reaching about 70% and an operating range between 300 and 500°C, first engine results were very disappointing showing efficiencies lower than 15% for all the operating points. Three guidelines for improving these results were identified and studied:

- The way the reductant is introduced in the exhaust, especially the discontinued HC delivery due to the injection pattern

- The gas velocity: unusual small GHSV values for automotive applications are needed to ensure a good NO_x conversion rate.
- The nature of the used reductant. Diesel fuel (ULSD) compared with decane lowers the efficiency, but synthetic Diesel fuel (SD) and, moreover, ethanol, largely improve it, especially for high GHSV.

INTRODUCTION

Compression Ignition Direct Injection (CIDI) and Spark Ignition Direct Injection (SIDI) engines are well-known and recognized for their high CO₂-saving potential. However, their lean-burn combustion yields to large amounts of NO_x emissions [1]. If Exhaust Gas Recirculation (EGR) and optimized combustion have been developed and used since the end of the 90's, these two technologies are now reaching their limits.

OEMs and suppliers actually work on DeNO_x aftertreatment technologies. Urea-SCR is definitely the most efficient one (>95%), on a large range of temperature (200-500°C), without any major issue on aging and poisoning [2][3][4]. The challenges remain (i) on an accurate control with a good understanding of the catalyst behavior versus all influent parameters [5], (ii) on the reductant cost and delivery method and (iii) on the global cost and packaging of the solution: efforts have to be made on sensors and actuators accuracy and reliability [6][7][8]. That high potential allows moving the NO_x / fuel economy trade-off more on the consumption side and having some significant CO₂ savings, from -2 to -5% [9].

Very impressive progresses have been made recently on Lean NO_x Traps (LNT) [10][11]. The efficiency can reach 90% between 250 and 450°C and the packaging is easier than for a urea-SCR system. The drawbacks are (i) the versatile price of the solution due to the PGM market, (ii) the management of NO_x / SO_x purges and (iii) the aging and the irreversible sulfur poisoning. Moreover, the lean/rich switches induce an extra fuel consumption (+1 to +2%) and the solution is not applicable on all the engine operating range, what could be an issue for some driving cycles.

In that context, HC-SCR appears as a credible alternative. The major issue concerning the formulation of the active phase relates to the selectivity and especially the compromise between HC oxidation and NO_x removal. For instance, the ion-exchanged base metal zeolite catalysts (e.g., Cu-ZSM-5) have a very low NO_x activity on the considered temperature range. PGM-containing catalysts have a good NO_x activity but in a very narrow temperature range [12]. The use of Silver on Alumina (Ag-Al₂O₃) is now recognized as the best solution for the HC-SCR thanks to its good selectivity on a large temperature range [13][14]. The most recent studies show encouraging results on a Synthetic Gas Bench (SGB), even if the efficiency strongly depends on the nature of HC being used [15]: paraffins, especially long-chain paraffins, yield to high efficiency, unlike aromatics. For low-temperatures, a continuous deactivation can be seen for most of the reductant used. Finally, alcohols like ethanol are very effective for NO_x conversion without any deactivation issue, despite a rather high selectivity to ammonia. However, a NH₃-SCR catalyst may be usefully fitted downstream of the HC-SCR one [16].

The RedNO_x project focuses on the development of innovative formulations to improve both the low-temperature activity and the selectivity of the catalyst. The target application is a diesel powered passenger car. The engine-out NO_x are supposed to be low with a low exhaust flow (high EGR-rate). Therefore, the reductant delivery has to be very accurate for very small injected quantities.

For those reasons, the transition from lab to engine has to be closely studied. Particularly, what are the prerequisites for a successful adaptation ? The paper focuses on this specific work, with the help of CFD-modeling and advanced measurement facilities.

The involved partners concerning that part of the project are PSA Peugeot-Citroën as end-user and exhaust-line designer, IRMA Technologies for catalyst prototyping and laboratory testing and IFP Energies nouvelles for the engine bench tests.

CATALYST

A state-of-the-art catalyst has been prototyped by IRMA, thanks to an extensive literature study [17]. A slurry made of 2% Ag on alumina has been prepared and coated at 150 g/L on a cordierite monolith of 400

psi. Two parts have been prepared, one for laboratory testing (25 cm³) and the second one for the engine test-bench (2.5L).

The main characteristics of the designed catalysts are summarized in the Table 1 hereunder.

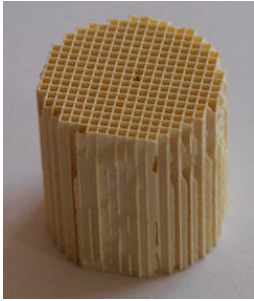
Support	Cordierite 400 cpsi
Slurry	2% Ag on Alumina 150 g/L
 Diameter : 1" Length : 2" Volume : 0.025 L	 Diameter : 5.66" Length : 6" Volume : 2.5 L

Table 1: Characteristics of the catalyst

REDUCTANTS

Different reductants have been used for the tests :

- Decane, chosen for the in laboratory tests, since paraffins compose more than the half of european Diesel fuels
- Ultra-Low Sulfur Diesel fuel (ULSD). It is mainly composed of n-paraffins, naphtens and of some aromatics.
- Synthetic Diesel fuel (SD), only used for some engine tests. This fuel, produced by the Fischer-Tropsch process from gas (GtL) has interesting properties: it is mainly paraffinic and the mean molecule is lighter than ULSD's one.
- Ethanol, possible reductant for some applications

The main properties of these four reductants are summarized in the Table 2.

		ULSD	SD	Ethanol	Decane
Mean Molecule		CH _{1.886}	CH _{2.15}	C ₂ H ₅ OH	CH ₃ (CH ₂) ₈ CH ₃
C		85.9	84.8	52.1	84.5
H		13.5	15.2	13.1	15.5
O	%wt	0.6	<0.5	34.7	0
NCV	kJ/kg	42920	43979	26800	
Density	kg/m ³	837	770.2	789	730
Comments		B5	GiL	99% pure	99% pure
Distillation Curve (°C)	5%	167	166	-	-
	50%	277	249.9	-	-
	100%	354	327.8	79	174

Table 2: Characteristics of the reductants

LABORATORY TESTS

For laboratory tests, the catalyst sample is fitted in a reactor installed in a controlled oven.

The tests have been performed in a diesel-like feed gas, described in Table 3.

NOx (ppm)	O ₂ (%)	H ₂ O (%)	CO (ppm)	H ₂ (ppm)	CO ₂ (%)	HC/NOx
400	8	10	500	167	10	3/6/9

Table 3: Laboratory feed gas composition

Some H₂ has been added to the feed gas to respect a 3/1 ratio between CO and H₂. This weak amount has an slight influence on the low temperature activity of the HC-SCR reaction (Figure 1).

HC on NOx ratio is defined as the ratio between HC (in ppmC1) and NOx (ppm) upstream of the catalyst. It is one of the main setting parameters of the HC-SCR process.

The reductants are delivered by a precision volumetric pump and vaporized in an in-house system.

Two gas hourly space velocities (SV) have been tested: 30000 and 60000 h⁻¹.

The first results were obtained with decane and the lowest SV. In Figure 1 is plotted the DeNOx efficiency behaviour for two feed gases with and without H₂.

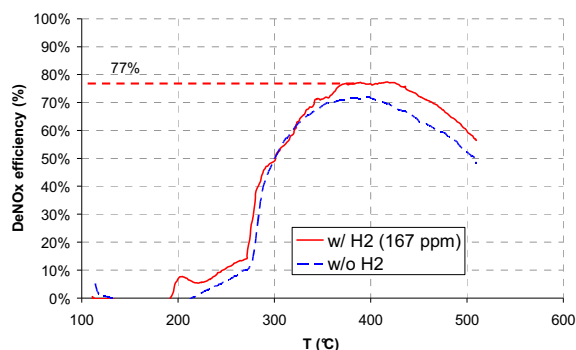


Figure 1: Laboratory NOx reduction efficiency, SV=30000 h⁻¹ (decane), feed gas with and without H₂

The results are consistent with the literature: the prototype catalyst demonstrates a peak NOx efficiency of 77% for a temperature between 380 and 420°C (for a feed gas containing 167ppm H₂). More generally, the conversion is higher than 60% over a 180°C wide range between 320 and 500°C. However, if the conversion ratios are correct, the low-temperature activity (<270°C) remains very low. This point is clearly an issue for a diesel-engine application.

Moreover, increasing the space velocity to values more usual of vehicle applications has a dramatic impact on the conversion results of the catalyst, as shown on Figure 2.

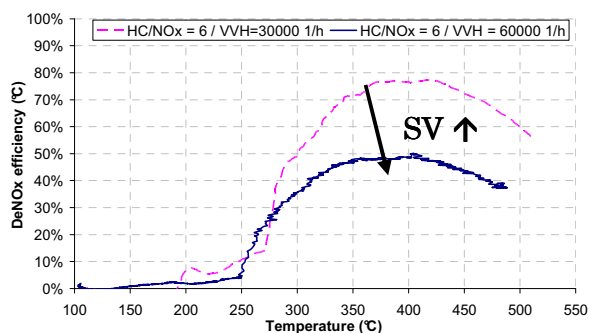


Figure 2: Laboratory NOx reduction efficiency as reductant, for SV=30000 h⁻¹ and SV=60000 h⁻¹ (decane)

The peak efficiency value decreases from 77% to less than 50% for a 60000 h⁻¹ SV.

The second factor that was swept is the HC on NOx ratio, between 3 and 9. Figure 3 shows the influence of that parameter on the laboratory results.

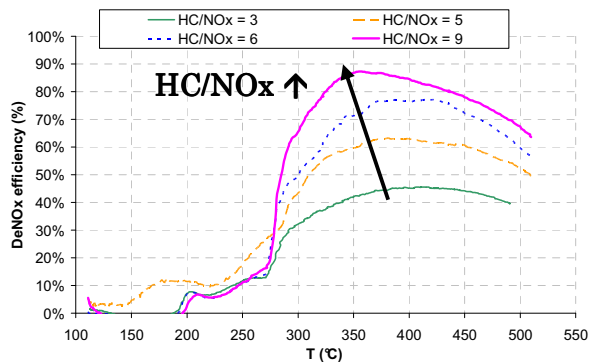


Figure 3: Laboratory NOx reduction efficiency for different HC/NOx ratios, SV=30000 h⁻¹ (decane)

As foreseen, the HC on NOx ratio is a key factor: if for the high temperatures the efficiency increases with the HC on NOx ratio, for the lowest temperature, the optimum setting is somewhat different. Moreover, the HC efficiency and the HC slip have to be taken in account. As the HC efficiency remains quite the same for all the HC on NOx ratios (See Figure 4) the HC-slip increase linearly with the HC on NOx ratios. That setting parameter should thus be chosen based on a