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Cerium oxide catalyzed DPF: lowering the soot combustion temperature

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Research team presentation

1/ CTAG: Galician Automotive Center

Engine component testing

2/ University of Alicante

Catalyst laboratory. Department of Inorganic Chemistry

3/ University of Vigo

Synthesis, Spectroscopy and Simulation

Research team presentation

Equipment, experts and knowledge from different branches joined together in the development of this project. Chemists, testing engineers and simulation engineers are working together to implement the basic formulation and lab scale work in real engine conditions.

X-ray difraction

Engine Dynamometer + gas analyzer

SEM & TEM microscopes

DRFTIR spectrometer

Gas mixer with mass spectrometer

Smoke meter

Gas chromatograph

Reactor connected to gas flow controllers and gas analyzer

Background: Emissions legislation and trends

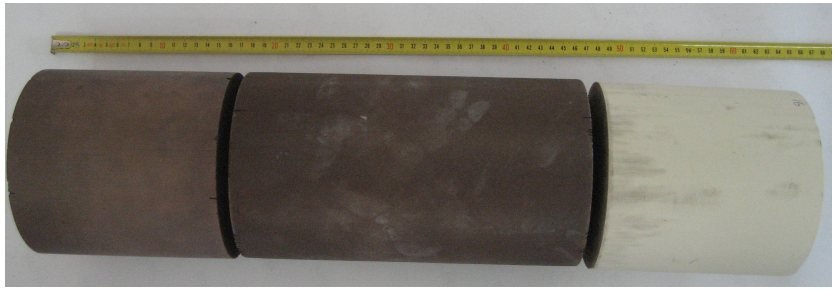
EU Passenger Cars (Diesel Engines): Over time emission legislation are getting tighter and tighter, specially for reduction of NOx and Particulate Matter

			EU-1	EU-2	EU-3	EU-4	EU-5	EU-5+	EU-6
			1992	1996	2000	2005	2009	2011	2014
Compression Ignition Engines (Diesel)	CO	mg/km	2720	1000	640	500	500	500	500
	HC + NOx	mg/km	970	700	560	300	230	230	170
	NOx	mg/km			500	250	180	180	80
	PM	mg/km	140	80	50	25	5	4,5	4,5
	PN	#/km						6E11	6E11

Euro 5: 80% reduction in the limits of particulate matter. As a result of implementation of Euro 5 legislation, new model Diesel vehicles require a PM filter to meet new emissions target

Background: Emissions legislation and trends

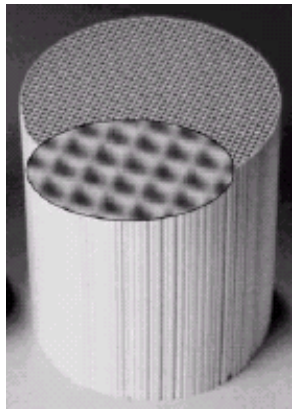
Euro 6: almost 56% reduction in NOx limits. For achieving this new emissions targets passenger car will include new technologies. Enhanced combustion, high pressure and low pressure EGR and after-treatment systems must be implemented to meet this requirements



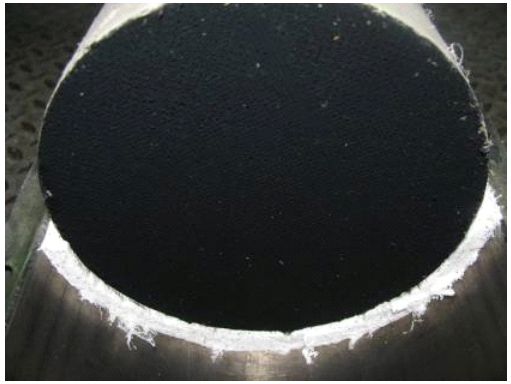
DOC DPF SCR

DPF: Problem definition and actual challenges

DPF system removes particulate matter from diesel exhaust by physical filtration. The most typical configuration is a ceramic honeycomb monolith, made of silicon carbide, aluminum titanate or cordierita.



This filters accumulate particulate until a maximum counterpressure is achieved. This is known as the maximum PM loading or soot mass limit.



Excess of soot in the DPF leads:

- Increase pressure drop for the same exhaust flow
- Decrease engine performance
- Increase fuel consumption (increase CO2)

DPF: Problem definition and actual challenges

DPF must be cleaned out, intermittently or continuously before achieving soot mass limit.

This regeneration can be:

- Active: by means of in cylinder post injection or by direct injection of diesel into the exhaust stream. (>600ºC are needed for soot combustion)

- Passive: DPF systems that are able to regenerate themselves using only the exhaust gas stream, without additionally energy inputs, are known as passive safety systems. The soot is burned off due to the following mechanism:

- O2 combustion $[C]+O_2 \rightarrow CO_2$

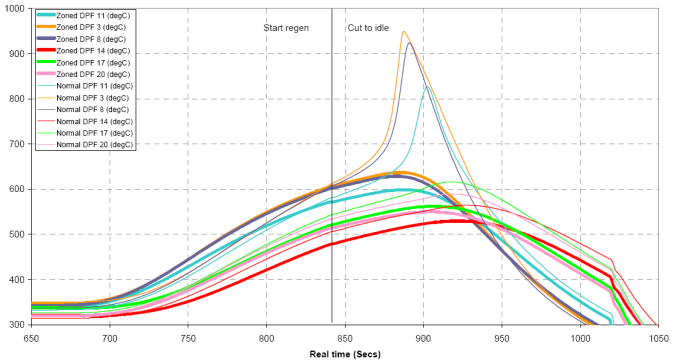
- NO2 assisted combustion $\rightarrow [C]+2NO_2 \rightarrow CO_2+2NO$

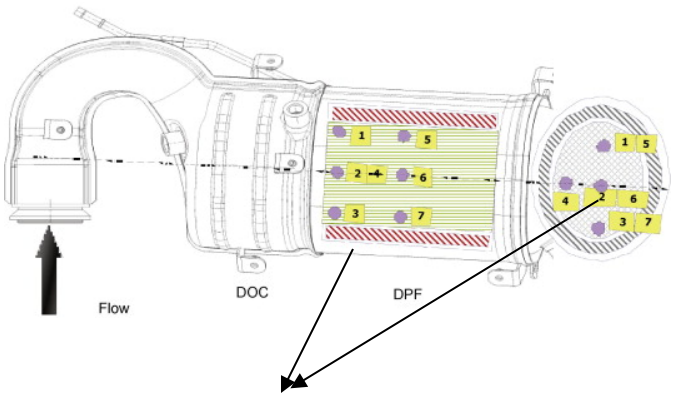
DPF: Problem definition and actual challenges

Active regeneration disadvantages:

- Very high temperatures inside DPF (1000ºC and even more temperature has been reported). When the DPF is regenerated, and due to the unevenly distribution of soot inside the DPF, high temperature gradients are produced. This produces high thermal stress in the ceramic monolith and the need of using expensive materials like silicon carbide and maintenance issues

- Additional diesel required



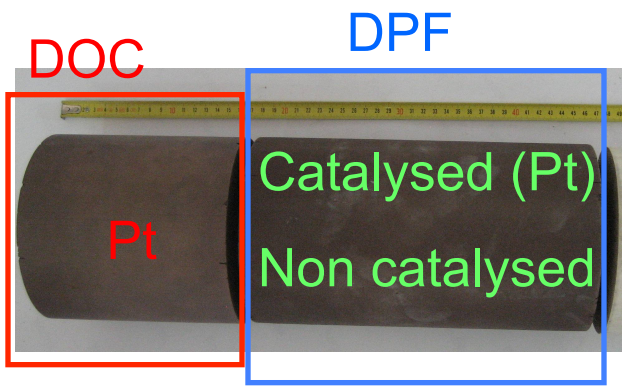


Thermocouples

DPF: Problem definition and actual challenges

Passive regeneration disadvantages:

- **High NOx:PM ratio. DOC to oxidize NO to NO_2**
- **With low exhaust temperatures Pt must be applied to the DPF**



Basic equation on DOC:

NO+1/2O2→NO2

CO+1/2 O2→CO2

HC+O2→CO2+H2O

Basic equation DPF (NO2 assisted combustion)

[C]+2NO2→CO2+2NO

Proposal: Cerium oxide-catalyzed DPF

- **Intense research effort has been carried out during the last decade in order to replace Pt by cheaper actives phases, and cerium oxide is one of the most promising options.**

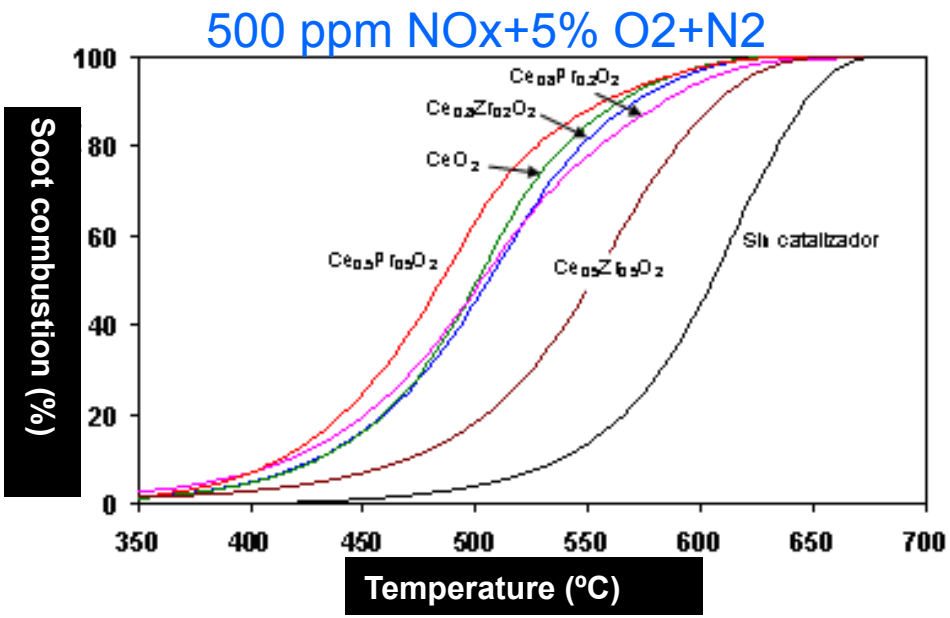
- **Advances in preparation of both pure and doped cerium oxides, including zirconium and praseodymium or lanthanum, among other has been made at laboratory scale in order to find the best formulation (high activity and thermal stability)**

- **Scaling up this laboratory scale studies to a real engine exhaust is not obvious due to poor soot-catalyst contact. As far as we know, the ceria-catalysed regeneration of DPF´s in real diesel exhaust stream has not been reported, this being the main goal of this study.**

Proposal: Cerium oxide-catalyzed DPF

Lab scale research

- **Several cerium based (pure and doped) catalyst were tested in order to find best formulations**
- **Soot combustion test were performed at lab scale with a gas stream of 500 ppm NOx+5% O_2+N_2:**

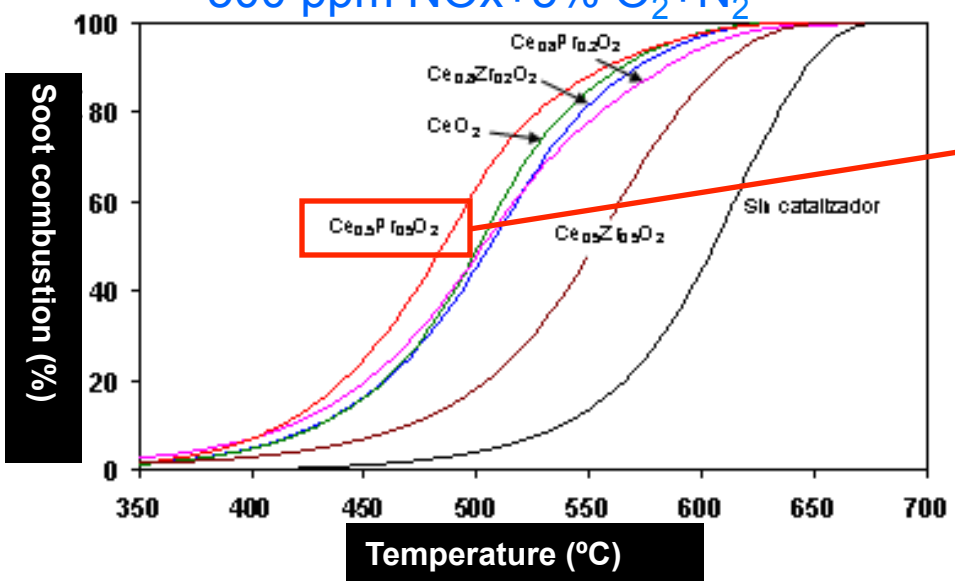


Proposal: Cerium oxide-catalyzed DPF

Results and discussion:

- **Catalytic activity is modified when doped**
- **The doping effect is different depending on applied metal (Pr or Zr) and the concentration of it**
- **Among all the formulations studied the best results was the cerium oxide doped with Praseodymium**

500 ppm NOx+5% O_2+N_2



$Ce_{0.5}\,\mathrm{Pr}_{0.5}\,O_2$

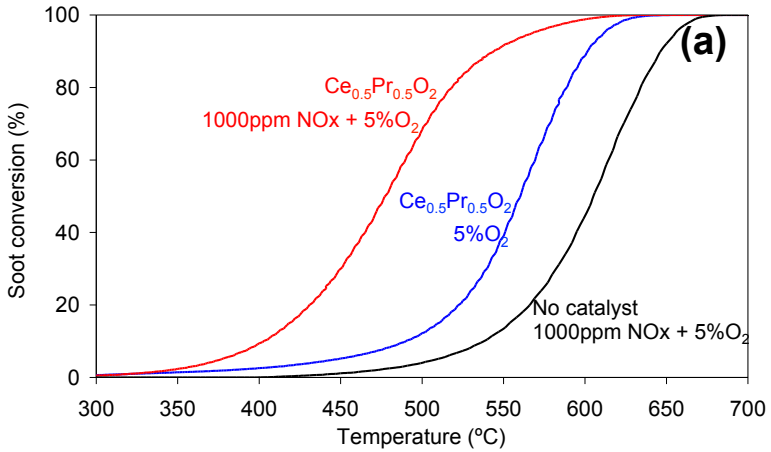
Lower soot combustion temperature

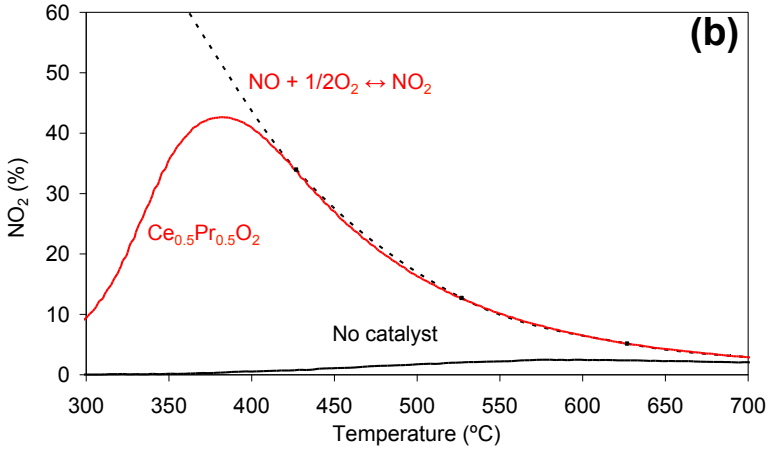
Proposal: Cerium oxide-catalyzed DPF

Soot combustion mechanism

In order to obtain additional information about the soot combustion mechanism, soot combustion experiments were performed at lab scale with powder. Figure (a) compiles soot combustion profiles obtained with two O2 containing gas mixtures, with and without NOx and figure (B) shows the NO2 production profiles in soot-free experiment performed with NOx/02

Remark: 20 mg of soot was used (Printex U soot)





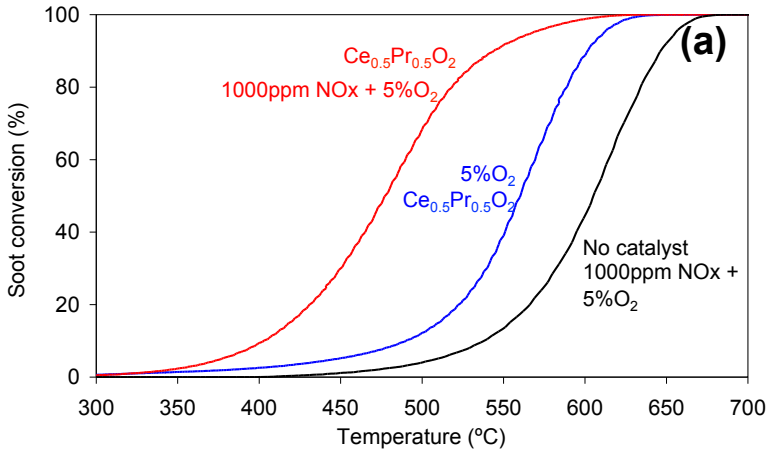
Proposal: Cerium oxide-catalyzed DPF

Soot combustion mechanism discussion $Ce_{0.5}Pr_{0.5}O_2$

According to **red line**, the cerium oxide is able to oxidise NO to NO_2 at lab conditions, with maximum production at around 400 ºC. This reduce the soot combustion temperature due to the NO_2 assisted combustion (450ºC)

Black line corresponds to O_2 combustion of soot which is produce, as expected, at around 600ºC

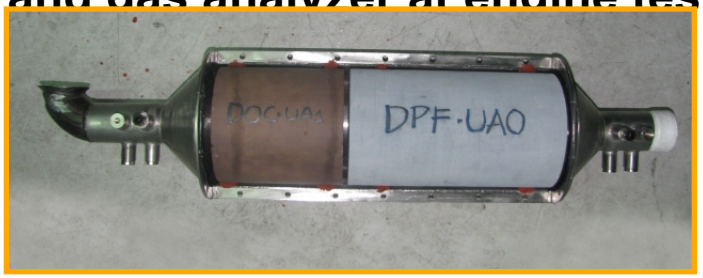
Blue line correspond to "active oxygen" soot combustion mechanism. This mechanism is related whit the capacity of certain oxides, like those of ceria, to capture O_2 molecules and yield highly reactive oxygen radicals. Therefore there is a combustion temperature reduction due to this combustion mechanism



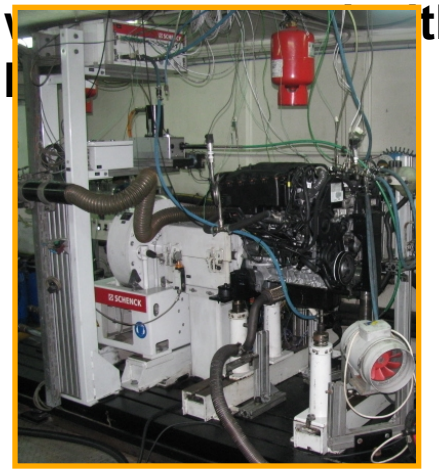
Proposal: Cerium oxide-catalyzed DPF

Scaling up and dynamometer testing on Euro V engine:

- **Cerium oxide doped $Ce_{0.5}\,\mathrm{Pr}_{0.5}\,O_2$ was used for coating of commercial honeycomb monolith (14,4 cm diameter, 14 cm length and 400 cpsi of cell density)**
- **Powder catalyst were prepared by air calcination at 500ºC of a mixture cerium and praseodymium nitrates. Water solution were prepared with the metal nitrates, which were decomposed by 500ºC air calcination**
- **Canning was designed and implemented in Euro V diesel engine (1.6 L 4 cylinders)**
- **Opacity and exhaust gases composition w th smoke meter and gas analyzer at engine test cell**



Cerium oxide-catalyzed DOC + DPF

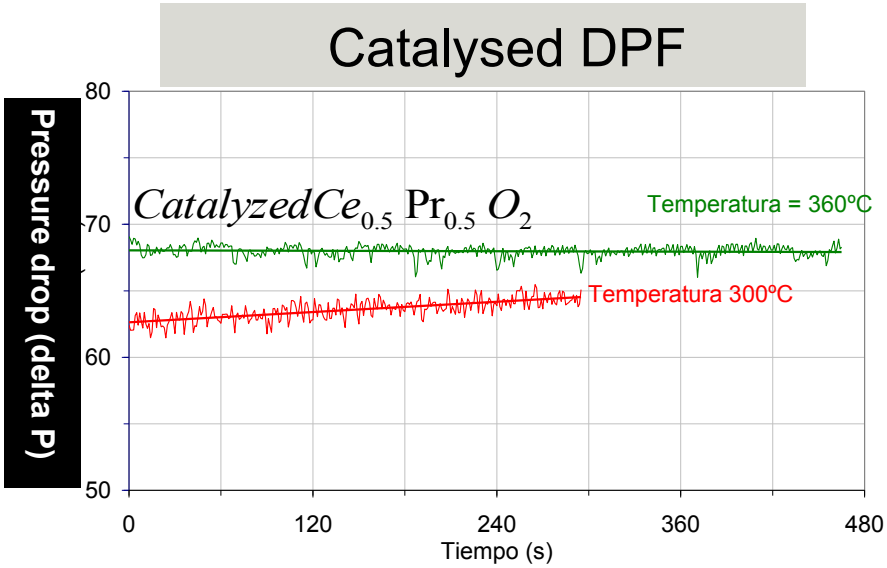


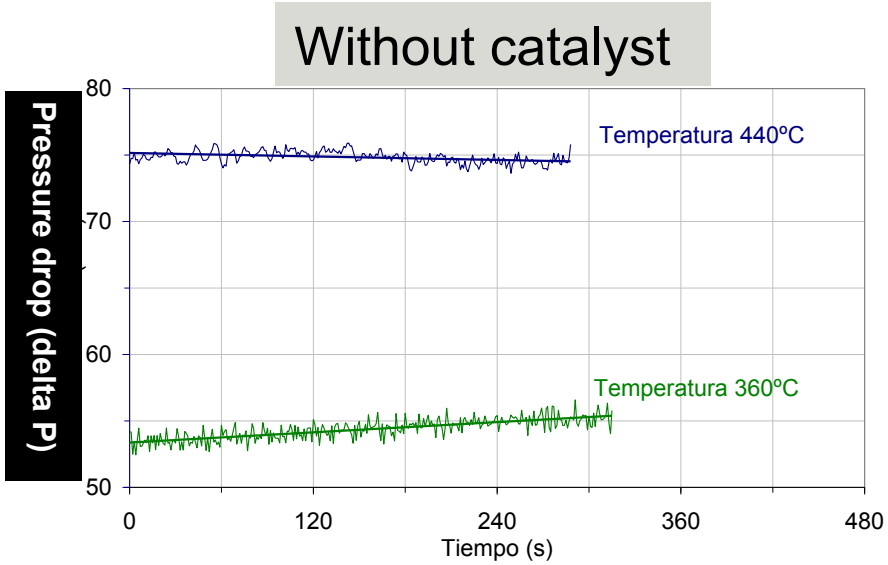
Engine test cell

Proposal: Cerium oxide-catalyzed DPF

Soot loading test

- Several repetition of soot loading was performed without catalyst free DPF and catalyzed DPF in order to understand soot temperature regeneration (based on pressure drop stabilization).
- Catalyzed DPF has 100ºC lower soot combustion temperature than non catalyzed DPF





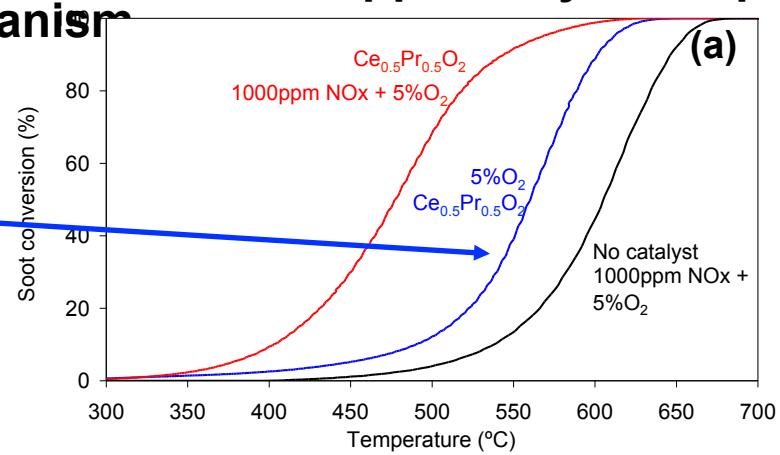
Proposal: Cerium oxide-catalyzed DPF

Cerium oxide catalyzed DOC

- Several test were performed at the same temperatures and similar residence times for faster comparison whit lab scale test. This temperatures and flows were controlled by means of torque and rpm.

- The NO conversion to NO_2 is very low and even null in some engine conditions. This allowed concluding, opposite to that observed at lab scale tests, that soot combustion in real exhaust is not based on the NO_2 assisted mechanism. This is apparently explain by the existence of inhibitors, mainly water and/or CO_2 which are not present in lab scale stream

- However engine testing showed low temperature combustion. Active oxygen soot combustion is apparently the predominant soot combustion mechanism



Proposal: Cerium oxide-catalyzed DPF

Summary:

- **With this initial study we prove the Cerium oxide can be implemented in real DPF design lowering soot temperature combustion.**

- **Cerium oxide are cheaper than Pt, which is the common precious metal used for the catalyzed DPF design (1:1000). It is also widely assumed that the PT prices in the future market will be even higher due to increasing demands**

- **This is a initial project with limited funding destined to it. There are still open points to low the soot temperature using this concept (changing oxides, concentrations, formulation…)**

SCR: Problem definition and actual challenges

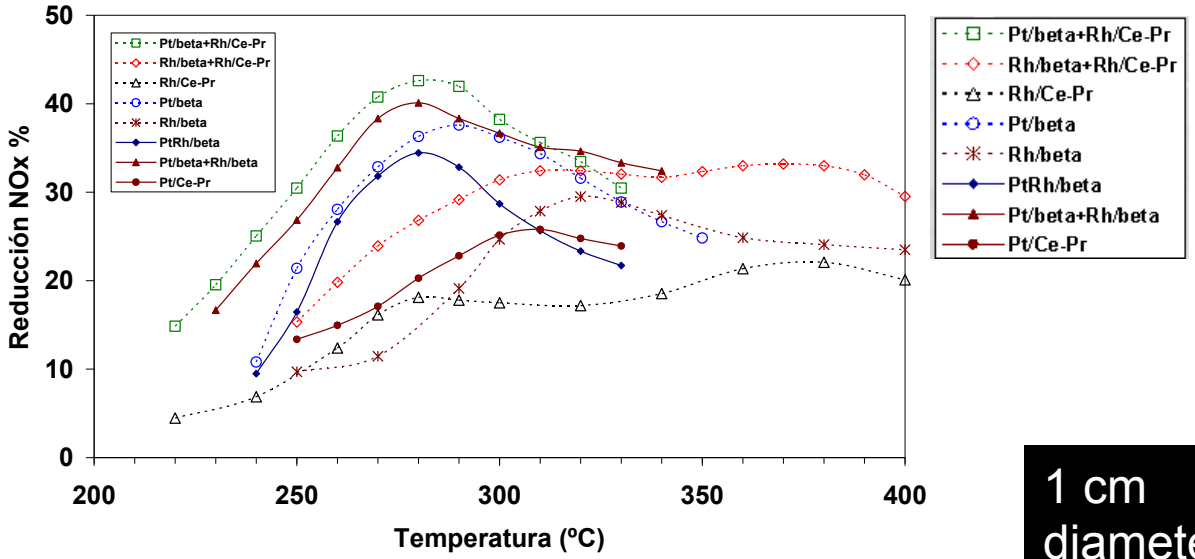
- **To meet future euro VI legislation, after-treatment system for reducing NOx should be implemented**

- **It is widely implemented the use of UREA (reductant) to enable the chemical reaction**

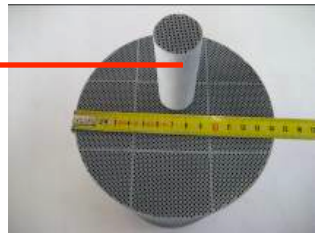
- **A new fluid and circuit (including tank and hoses) must be implemented in the engine layout and refilling of this fluid must be done periodically**

PT- Beta zeolita SCR with diesel working as reductant

- **Lab scale study: Small monolith (D=1cm) were prepared to test at lab scale the performance of different SCR. The catalyst studied were noble metals (Pt and/or Rh) and promoters like cerium-praseodymium oxide and beta-zeolite**



1 cm diameter



PT- Beta zeolita SCR with diesel working as reductant

Lab scale results and discussion

- **Highest NOx conversion obtained was Pt/beta with Rh/ce-Pr**

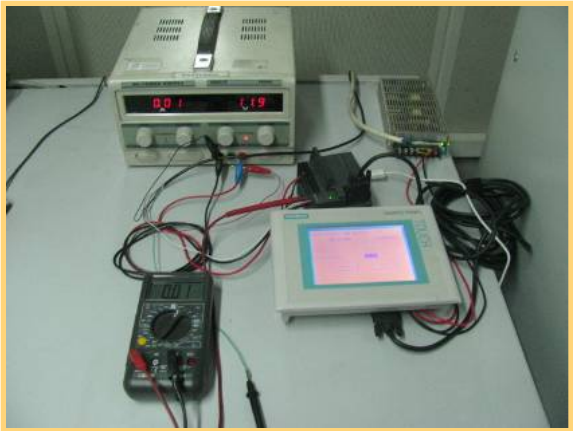
- **When comparing Pt and Rh catalyst, as general trend Pt catalyst produces higher NOx conversion rates but higher N_2O (greenhouse effects).**

- **If temperature of gases are higher than 350ºC the deN_2O will be not necessary. If reduction of N_2O is necessary below this temperature, double bed catalyst is needed. One de-NOx (Pt containing) and de-N_2O (Rh containing)**

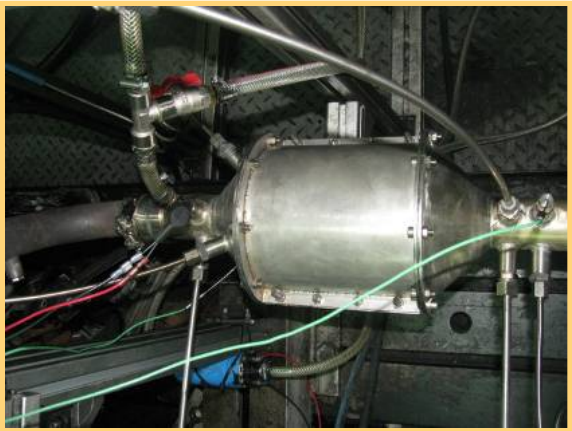
PT- Beta zeolita SCR with diesel working as reductant

<u>Scaling up and dynamometer testing on Euro V engine:</u>

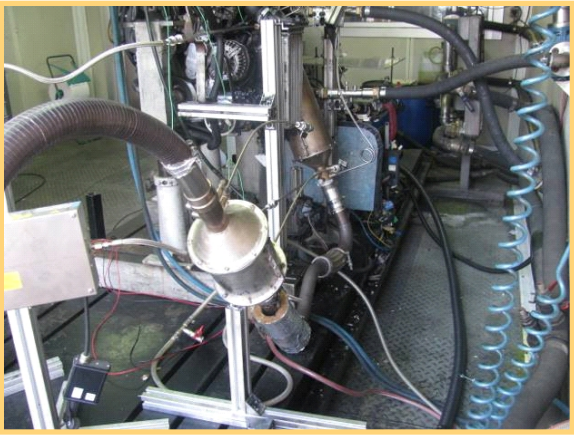
- **One monolith coated with Pt-Beta zeolite (dip coating method)**
- **A system for diesel spray in the SCR inlet was implemented**
- **Removable SCR canning was design for monolith**



Diesel spray device



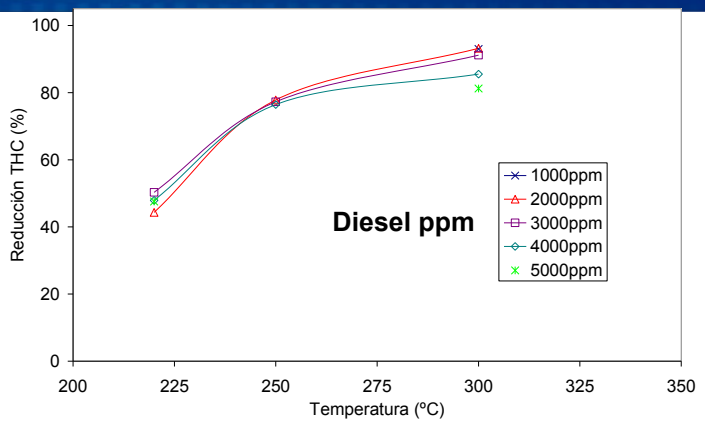
SCR canning



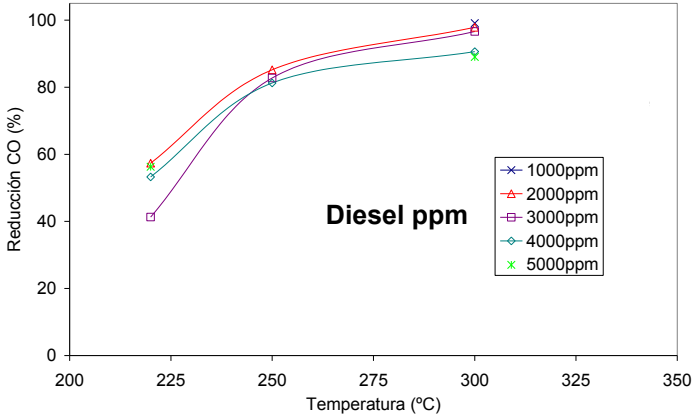
Experimental SCR in engine

PT- Beta zeolita SCR with diesel working as reductant

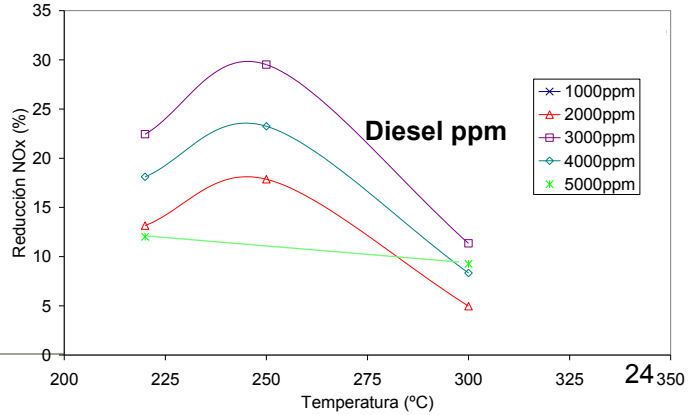
- **Maximum NOx reduction of 30% with 3000 ppm of diesel spray**



- **Maximum NOx conversion at 250ºC (NOx selectivity)**



- **Oxidation of CO and HC, increasing the conversion with the temperature**



Conclusions and further work

- The active phase $Ce_{0.5}Pr_{0.5}O_2$ has been loaded on a commercial SiC DPF, improving filter regeneration, with lower cost than using noble metals

- Soot combustion mechanism in real diesel exhaust is based in active O_2 mechanism, not in NO_2 assisted mechanism

- The SCR prototype is able to reduce an amount of NOx and oxidize the CO and HC at the same time.

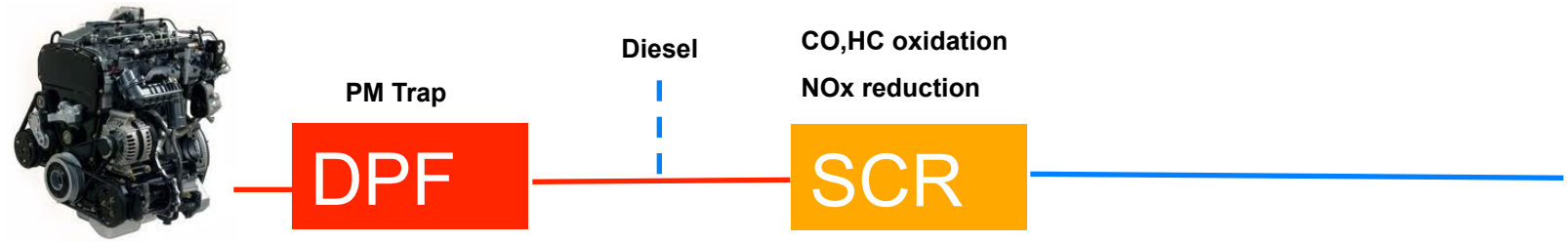
- There are still open points to be improved in order to achieve higher efficiency and conversion rates (improving spray turbulence, distribution, catalyst formulation,….)

Conclusions and further work

- ¿Is a new after treatment concept without DOC feasible ?

Conventional concept

Proposal



THANK YOU

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