Accepted Manuscript
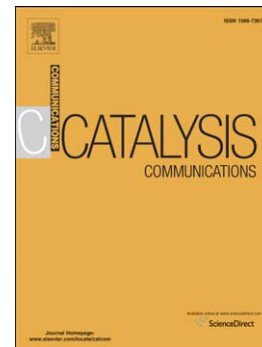
Proof of concept of the SCR of NOx in a real diesel engine exhaust using commercial diesel fuel and a full size Pt/beta zeolite/honeycomb monolith

M. Valencia, E. López, S. Andrade, M.L. Iris, V. Rico Pérez, C. Salinas Martínez de Lecea, A. Bueno López

Please cite this article as: M. Valencia, E. López, S. Andrade, M.L. Iris, V. Rico Pérez, C. Salinas Martínez de Lecea, A. Bueno López, Proof of concept of the SCR of NOx in a real diesel engine exhaust using commercial diesel fuel and a full size Pt/beta zeolite/honeycomb monolith, *Catalysis Communications* (2013), doi: 10.1016/j.catcom.2013.11.026

Proof of concept of the SCR of NOx in a real diesel engine exhaust using commercial diesel fuel and a full size Pt/beta zeolite/honeycomb monolith.

M. Valencia[1], E. López[1], S. Andrade[1], Iris M. L.[1], V. Rico Pérez[2], C. Salinas Martínez de Lecea[2], A. Bueno López[2,*].

[1] *Galician Automotive Technology Center,Testing Labs. Pol. Industrial A Granxa P.O. 36400 Parcela 249-250. Porriño-Pontevedra (Spain).*

[2] *Inorganic Chemistry Department. University of Alicante. Ap. 99 E03080. Alicante (Spain)*

Abstract

The Selective Catalytic Reduction (SCR) of NOx has been performed in a real diesel exhaust stream with commercial diesel fuel by using a full size home-made Pt/beta zeolite/honeycomb prototype catalyst. Fuel was injected upstream the catalyst to achieve total hydrocarbons concentrations between 1000 and 5000 ppm, and the SCR behaviour observed was similar to that typically reported in laboratory experiments performed with model hydrocarbons. Typical NOx removal volcano-shape profiles, with maxima at 250 ºC for all THC inlet concentrations, were obtained, with an optimum THC concentration of 3000 ppm.

Keywords: SCR; NOx; diesel pollution control; Pt catalyst; diesel fuel; honeycomb monolith.

---

* Corresponding author: agus@ua.es

1.- Introduction.

The main drawback of NOx removal on Diesel vehicles is the oxygen excess in the exhaust, and a reducing agent must be fed into the exhaust stream which must react with NOx in the presence of excess O_2. Different reducing agents have been studied, most of them at laboratory scale, including H_2, CO, different hydrocarbons, ammonia, urea, etc. [1-6].

In the SCR (Selective Catalytic Reduction) technology [2, 3], the reducing agent is continuously fed into the gas stream and a selective catalyst is used to promote the reaction of the reducing gas with NOx with respect to the unproductive direct O_2 combustion.

In the NSRC (NOx Storage and Reduction Catalyst) process [1-3], the NOx removal process is carried out in cycles of storage and reduction steps. During the storage steps, which occur in normal driving conditions, NOx is chemisorbed on a basic oxide present on the catalyst. During the reduction steps, the reducing gas is fed and reacts with the nitrogen compounds previously stored (and also with O_2).

The SCR technology with urea or ammonia is commercially available for heavy-duty vehicles [6], and the NOx removal technologies suitable for cars are now in a step of optimization and improvement [7]. Some previous articles reported NOx removal studies in real diesel exhausts [2, 8-13]. Copper and platinum titania based monolithic catalysts were tested for the reduction of NOx with hydrocarbons in real diesel conditions [10, 11], Ag/Al_2O_3 catalysts were tested for NOx reduction with ethanol in a real diesel exhaust [12] and Cu/titanium silicalite (TS-1) zeolite/cordierite honeycomb catalysts were studied

2

for the simultaneous removal of the NOx, hydrocarbons and CO emitted by a stationary diesel engine [13].

From a practical point of view the most convenient reducing agent would be diesel fuel, because it is already on board on the vehicle and additional tanks and filling facilities would not be required.

In one of our previous studies, the SCR of NOx was successfully performed with propene in a real diesel gas stream (in a power bench) by using a Pt/Al$_2$O$_3$ catalyst [9]. Also, it has been demonstrated in laboratory experiments that Pt/zeolite catalysts outperform the behaviour of Pt/Al$_2$O$_3$ due to the zeolites ability of maintaining a high concentration of hydrocarbon in the catalyst [14]. In previous studies, Pt/beta zeolite/honeycomb monolith catalysts, with 1 cm diameter substrates, were prepared and tested in our laboratory for SCR of NOx with propene [15, 16].

The goal of the current study is to demonstrate that the SCR of NOx can be performed in a real diesel exhaust stream by commercial diesel fuel and using a full size Pt/beta zeolite/honeycomb monolith catalyst.

2.- Experimental details.

2.1 Catalyst preparation.

A cordierite honeycomb monolith supplied by Corning was used as catalyst supports (14.4 cm diameter; 14 cm length; 400 cpsi).

Beta zeolite was loaded into the honeycomb monolith by dip-coating [17-19] with a water suspension of 9 wt.% commercial powder ammonia beta

zeolite (Zeolyst International), 0.4 wt. % surfactant (Teepol) and 0.2 wt.% binder (a 40 wt.% suspension of colloidal silica in water; Ludox AS-40).

To obtain a homogeneously dispersed mixture, the slurry was stirred with a high-shear mixer (UltraTurrax T50 from IKA Labortechnik) for 15 minutes at 1500 rpm. After 5 minutes stabilization, the slurry viscosity was measured with a viscometer SV10 from A&D, being 1.3 mPa·s. Using this viscosity, blowing the suspension excess with compressed air was not necessary.

The monolith was dipped into the slurry with a home-made dip-coater at a rate of 1.5 cm/min, both for monolith immersion into the slurry and to take it out. Four consecutive dipping steps were performed.

The coated monolith was dried overnight at room temperature while rotating in horizontal position. Afterwards, it was heat-treated in air in a furnace by heating from room temperature to 200 ºC at 1 ºC/min and from 200 to 500 ºC at 10 ºC/min, keeping the maximum temperature for 4 hours. The beta zeolite loading was 10.5 wt. % after calcination ($0.05 \ g_{zeolite}/cm^3_{monolith}$).

Finally, the beta zeolite-coated monolith was impregnated with a water solution of $[Pt(NH_3)_4](NO_3)_2$ (Alfa-Aesar) to obtain 1 wt. % Pt loading on zeolite basis. The amount of water used to dissolve the Pt precursor and to impregnate the monolith was the minimum amount that ensured no dropping upon impregnation. This amount was determined experimentally, being around 4.5 $g_{water}/g_{zeolite}$. 50% of the Pt solution was homogeneously dropped with a pipette to one of the end sides of the beta zeolite-coated substrate, and afterwards, the remaining 50% was dropped to the other one. The impregnated monolith was dried at 90 ºC in vertical position, changing the position of the monolith up-side-down every 30 minutes for 4 hours. After this time the monolith was apparently

4

dried and was kept overnight at 90 ºC in horizontal position. Finally, the monolith was calcined in air at 500ºC (heating rate 5ºC/min) keeping the maximum temperature for 2 hours.

2.2. Catalytic tests.

SCR experiments were performed in a engine test bench Horiba Titan S190, with the full size monolith loaded with Pt/beta zeolite and a 1.6 HDI diesel engine running with commercial diesel fuel (DIESEL e+, by Repsol) at 1100 rpm and different loading (torque between 45 and 83 N·m). Depending on the engine loading, the temperature at the entrance of the SCR catalysts and the gas composition ranged as indicated in Table 1.

In these experiments the whole exhaust stream was treated. The same diesel fuel used for running the engine was also used as reducing agent, being fed to the exhaust stream by a fuel injector located at the entrance of the metal holder used to fit the catalyst to the exhaust pipe (see Figure 1). The catalyst holder was designed and fabricated for this study. The holder is provided with five connections at the inlet part of the monolith catalyst, in order to connect a thermocouple, a pressure sensor, the fuel injection system and the two gas conductions connected to the gas analyzers and gas opacimeter, respectively. At the monolith catalyst exit, the holder is provided with four connections for a thermocouple, a pressure sensor and also two gas conductions connected to the gas analyzers and gas opacimeter, respectively

The fuel injection system consists of a fuel pump, a programmable touch screen, a programmable logic controller (PLC), and a low-pressure injector. Both the frequency and amount of fuel pulsed can be selected in order to ensure a precise control of the THC concentration in the inlet gas stream.

5

SCR experiments were performed by feeding different amounts of fuel in order to reach THC (total hydrocarbons) concentrations in the exhaust (measured at the entrance of the catalyst holder) in the range 1000-5000 ppm. The SCR experiments were extended until all engine parameters and gas compositions were at steady state.

Specific gas analyzers (Horiba Mexa 7170D) were used for gas composition monitoring (CO, CO_2, total hydrocarbons (THC), and O_2 were monitored).

3.- Results and discussion.

Figure 2 compiles the catalytic test results obtained in SCR experiments. THC and CO removal increased with temperature (Figures 2a and 2b, respectively) and NOx removal (Figure 2c) followed a typical volcano-shape profile, with maxima at 250 ºC for all THC inlet concentrations studied. The production of NO_2 (data not shown for the sake of brevity) by catalytic oxidation of NO is low in all experiments, that is, the NO_2 percentage with regard to total NOx is always lower than 10%. This behaviour is similar to that typically observed in laboratory experiments performed with model hydrocarbons [20-22]. Volcano profiles are usually originated by competitive reactions (fuel–NOx and fuel–O_2 in this case). NOx removal increases with temperature until a maximum value, because the fuel–NOx reaction rate increases with temperature, and above that temperature, the NOx reduction decreases because the fuel–O_2 reaction is favoured with regard to fuel–NOx [20-22]. In the experiments performed in the current study, it must be also taken into account

6

that the inlet NOx concentration increases with the exhaust temperature (see data on Table 1), and this also affects the shape of the NOx removal profiles on Figure 2c.

The temperature for maximum NOx removal (250 ºC) was only slightly higher than values previously obtained in laboratory experiments with 1 cm diameter Pt/beta zeolite/honeycomb monolith by using propene as model hydrocarbon (210-230 ºC) [15-16], confirming that the Pt/beta zeolite catalyst is a good candidate for low temperature NOx reduction with commercial diesel fuel.

The amount of fuel injected significantly affected NOx removal, and there was an optimum concentration at 3000 ppm THC inlet concentration, as observed in Figure 3. Only considering the *Le Chatelier's principle* one would expect a continuous increase of NOx removal with THC inlet concentration, but this only occurred below 3000 ppm THC. Two arguments have been proposed to explain the NOx removal decrease at high THC concentration [9]. In one hand, for the hydrocarbon-NOx reactions to occur on a catalyst surface the reactants must be chemisorbed on the catalyst, and a huge excess of one of the reactants (THC in this case) hinders the chemisorption of the remaining gases, inducing a certain poisoning effect. On the other hand, the hydrocarbon combustion reactions are highly exothermic, and the increase of temperature within the catalyst promotes the hydrocarbon-O_2 reaction, decreasing the selectivity of the process. This effect is evidenced in Figure 4, where the temperature at the catalyst outlet is plotted against the THC inlet concentration. In most experimental conditions, the gas temperature decreases within the catalytic bed, since most outlet temperatures are below the corresponding inlet

temperatures. However, an increasing trend was obtained with the THC concentration for experiments performed at the same inlet temperature due to the exothermic character of the THC combustion reaction, therefore affecting the SCR selectivity due to the formation of local hot spots within the monolith.

The results obtained in this study confirm that the SCR of NOx can be achieved by commercial diesel fuel in real light-duty vehicles with a Pt/beta zeolite/honeycomb monolith catalyst, therefore avoiding additional tanks on board which are required for some other reductants like urea or ammonia. After this proof of concept, next step for further studies would be to optimise the experimental variables in order to achieve NOx removal levels as high as possible, for instance optimizing the catalyst preparation, Pt loading, fuel injection, catalyst temperature control, utilization of several consecutive small catalysts instead of in a single bed with fuel injection before each catalyst, etc.

4.- Conclusions.

The results of this study demonstrated that the SCR of NOx can be performed in a real diesel exhaust stream with commercial diesel fuel by using a full size Pt/beta zeolite/honeycomb monolith catalyst.

The SCR behaviour observed in the real exhaust with commercial diesel fuel was similar to that typically reported in laboratory experiments performed with model hydrocarbons. Typical NOx removal volcano-shape profiles, with maxima at 250 ºC, were obtained, with an optimum THC concentration of 3000 ppm.

Acknowledgments

8

9

5.- References.

[1] W.S. Epling, L.E. Campbell, A. Yezerets, N.W. Currier, J.E. Parks II, Catal. Rev. 46 (2004) 163-245.

[2] A. Fritz, V. Pitchon, Appl. Catal. B-Environ. 13 (1997) 1-25.

[3] R. Burch, Catal. Rev. 46 (2004) 271-333.

[4] Y. Traa, B. Burger, J. Weitkamp, Micropor. Mesopor. Mat. 30 (1999) 3-41.

[5] P.L.T. Gabrielsson, Top. Catal. 28 (2004) 177-184.

[6] T. Johnson, Platin. Met. Rev. 52 (2008) 23-37.

[7] L. Xu, R.W. McCabe, Catal. Today 184 (2012) 83–94.

[8] M. Makkee, H.C. Krijnsen, S.S. Bertin, H.P.A. Calis, C.M. Van Den Bleek, J.A. Moulijn, Catal. Today 75 (2002) 459-464.

[9] G. Garrigós-Pastor, S. Parres-Esclapez, A. Bueno-López, M.J. Illán-Gómez, C. Salinas-Martínez de Lecea. Appl. Catal. A- Gen. 354 (2009) 63–71.

[10] C.U. I. Odenbrand, J. Blanco, P. Avila, C. Knapp. Appl. Catal. B- Environ. 23 (1999) 37–44

[11] J. Blanco, C.U.I. Odenbrand, P. Avila, C. Knapp. Catal. Today 45 (1998) 103-108

[12] C. Zhang, H. He, S. Shuai, J. Wang. Environ. Pollution 147 (2007) 415-421

[13] L. Li, J. Chena, S. Zhang, N. Guana, T. Wang, S. Liu. Catalysis Today 90 (2004) 207–213.

[14] M.V. Twigg. Appl. Catal. B-Environ. 70 (2007) 2–15.

[15] A. Bueno-López, D. Lozano-Castelló, I. Such-Basáñez, J.M. García-Cortés, M.J. Illán-Gómez, C. Salinas-Martínez de Lecea. Appl. Catal. B-Environ. 58 (2005) 1–7.

[16] A. Bueno-López, M.J. Illán-Gómez, C. Salinas-Martínez de Lecea. Appl. Catal. A-Gen. 302 (2006) 244–249.

[17] A.E.W. Beers, T.A. Nijhuis, F. Kapteijn, J.A. Moulijn. Microp. Mesop. Mat. 48 (2001) 279-284.

[18] A.E.W. Beers, R.A. Spruijt, T.A. Nijhuis, F. Kapteijn, J.A. Moulijn. Catal. Today 66 (2001) 175–181.

[19] A. E.W. Beers, T.A. Nijhuis, N. Aalders, F. Kapteijn, J.A. Moulijn. Appl. Catal. A-Gen. 243 (2003) 237–250.

[20] R. Burch, J.P. Breen, F.C. Meunier, Appl. Catal. B: Environ. 39 (2002) 283–303.

[21] J.M. García-Cortés, J. Pérez-Ramírez, M.J. Illán-Gómez, F. Kapteijn, J.A. Moulijn, C. Salinas Martínez de Lecea, Appl. Catal. B-Environ. 30 (2001) 399–408.

[22] J.M. García-Cortés, J. Pérez-Ramírez, J.N. Rouzaud, A.R. Vaccaro, M.J. Illán-Gómez, C. Salinas Martínez de Lecea, J. Catal. 218 (2003) 111–122.

Figure Captions

Figure 1. Photograph of the metal holder used for the full size SCR monolith catalyst, which is fitted in the exhaust pipe.

Figure 2. Catalytic results obtained at steady state with a full size Pt/beta zeolite/honeycomb monolith catalyst upon injection of different amounts of commercial diesel fuel versus temperature at catalyst inlet.

Figure 3. Effect of the amount of fuel injected on NOx removal.

Figure 4. Effect of the amount of fuel injected on catalyst temperature.

Table 1. Gas temperature and composition measured at the entrance of the monolith catalyst (without fuel injection) for different engine loading.

Exhaust gas flow (kg/h)	Torque (N·m)	GHSV (h^{-1})	Gas temperature ($^{\circ}$C)	O_2 (%)	CO_2 (%)	CO (ppm)	THC (ppm)	NO (ppm)	NO_2 (ppm)
17	45	9460	220	8	11	534	310	91	6
17	60	10035	250	7	12	320	375	218	0
18	83	11640	300	5	13	455	143	411	0
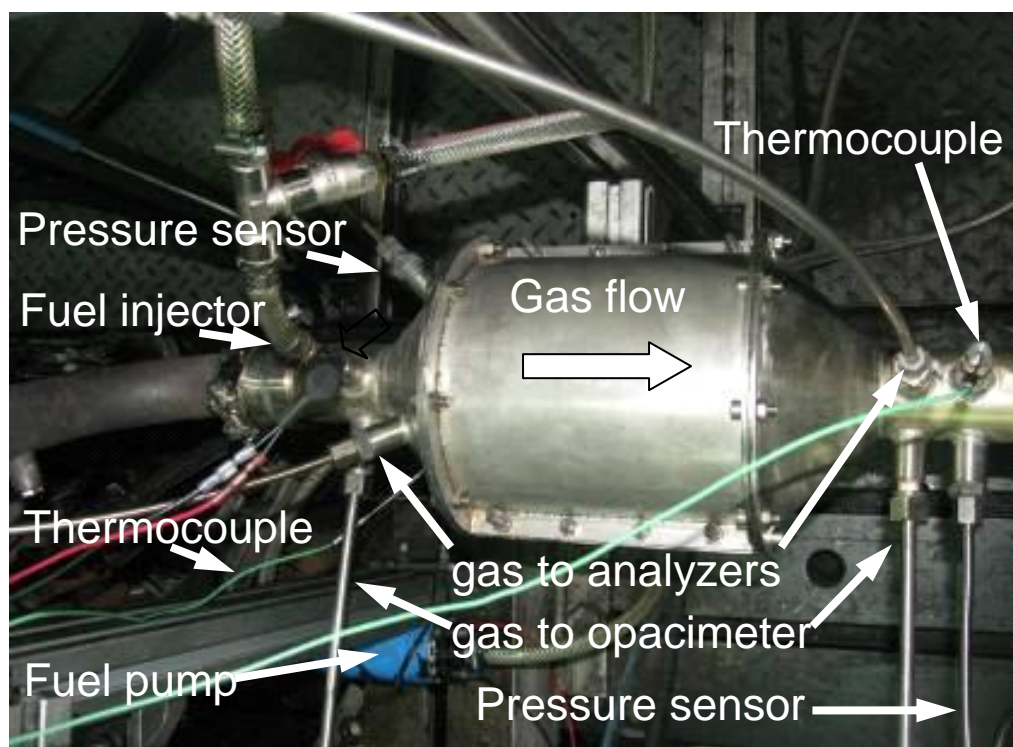
Figure 1.
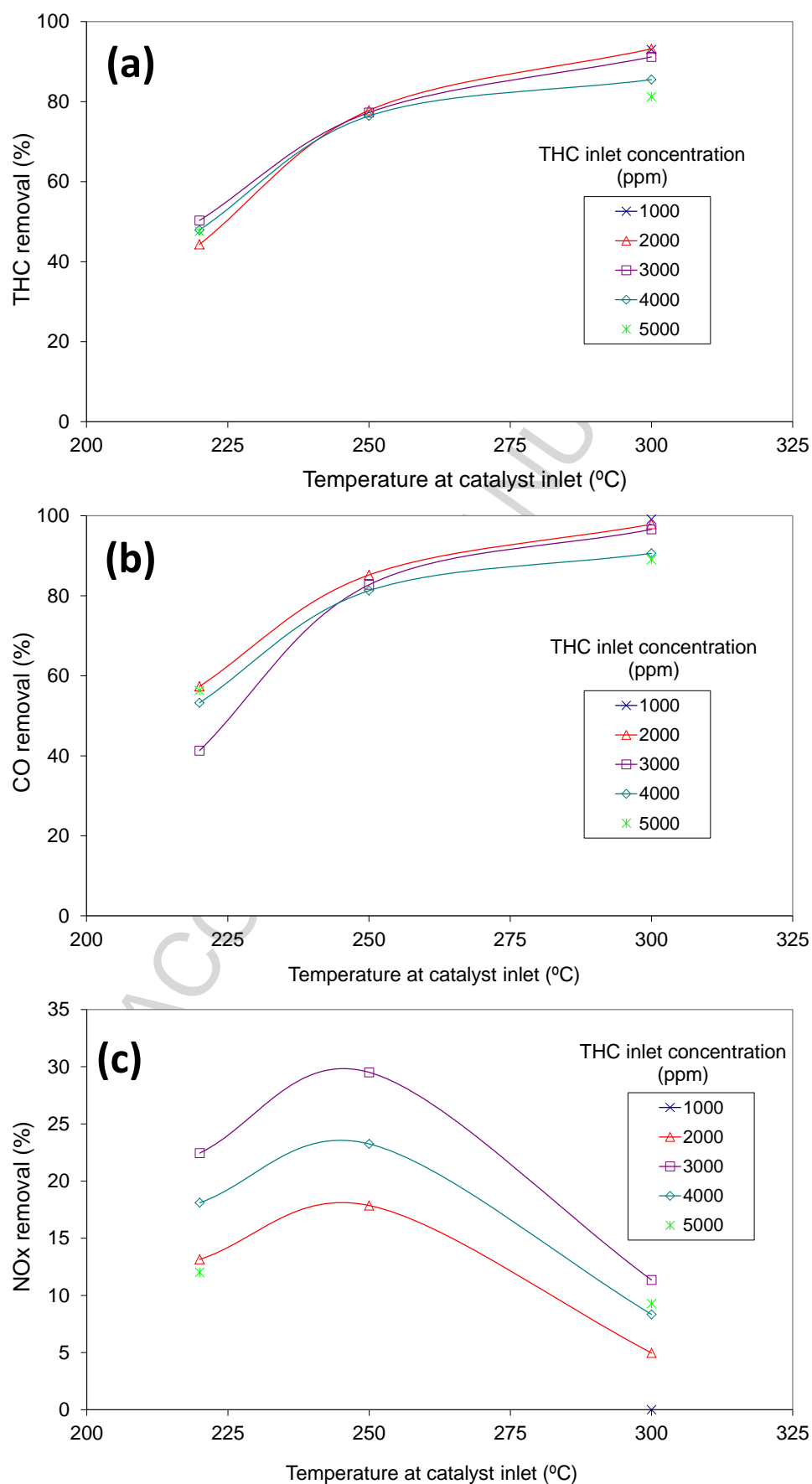
Figure 2.

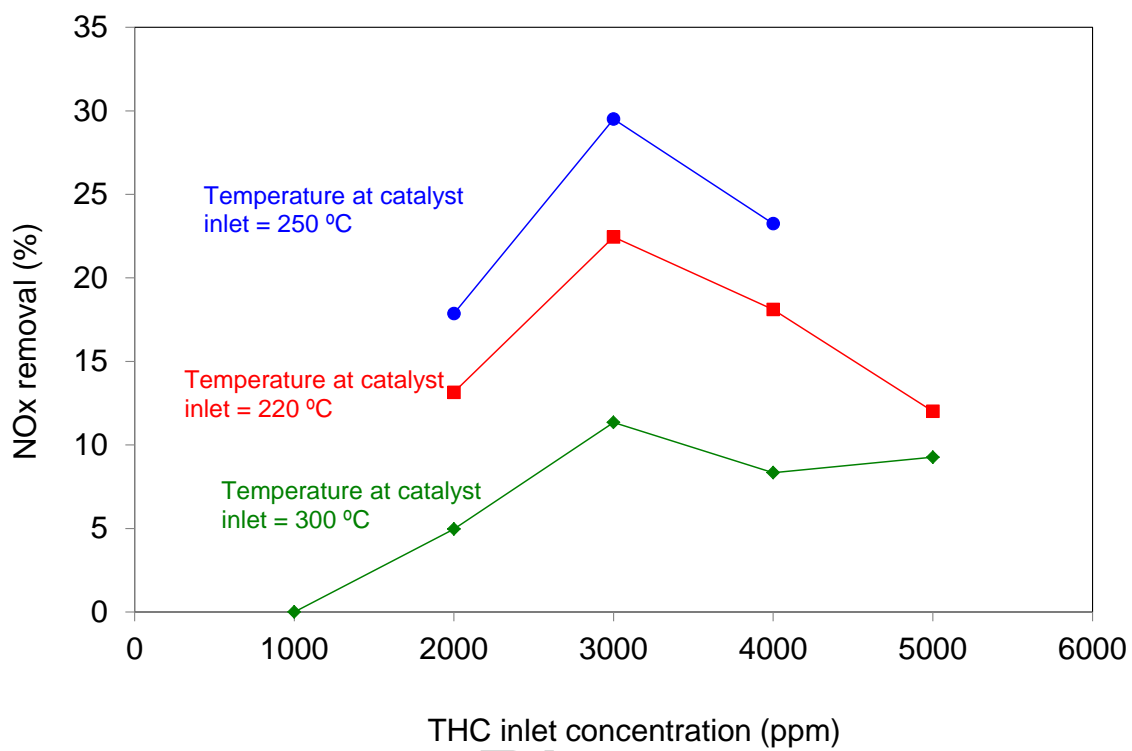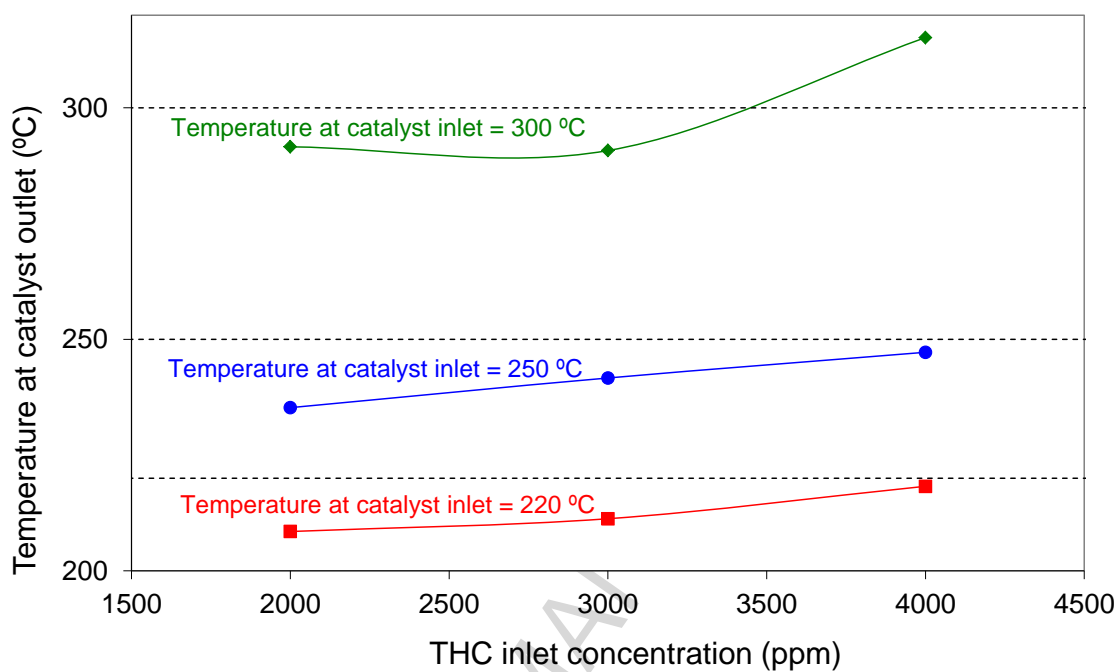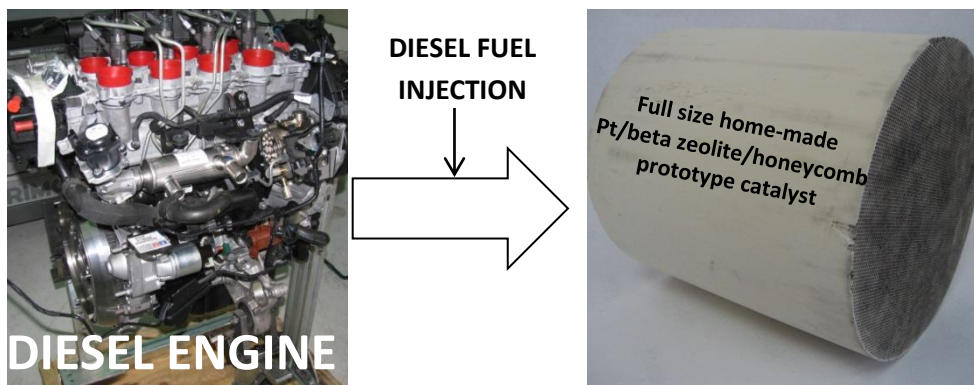**Figure 3.**

Figure 4.

Graphical Abstract

Research highlights

- SCR of NOx has been performed in a real diesel exhaust with commercial diesel fuel

- A full size Pt/beta zeolite/honeycomb monolith catalyst has been prepared and used

- The SCR behaviour was similar to that reported for model hydrocarbons at laboratory

- NOx removal volcano-shape profiles, with maxima at 250 ºC, were obtained.

- The optimum THC concentration was 3000 ppm.