

Increased NO2 concentration in the diesel engine exhaust for improved Ag/Al2O3 catalyst NH3-SCR activity

Wang, W., Herreros, J. M., Tsolakis, A. and York, A. P. E.

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Wentao Wang^a, Jose. M. Herreros^a, Athanasios Tsolakis^a* and Andrew P.E. York^b

^aSchool of Mechanical Engineering, University of Birmingham, Edgbaston, B15 2TT, UK

^bJohnson Matthey Technology Centre, Blount's Court, Sonning Common, Reading RG4 9NH, UK

Abstract

Increasing the NO₂ availability in some aftertreatment systems enhance their performance in reducing pollutants from internal combustion (IC) engines but result in significant fuel economy and CO₂ emissions penalties. The presence of NO₂ in the engine exhaust gas enhances the regeneration of the Diesel Particulate Filters (DPFs) and can improve the activity of the catalysts in reducing NOx emissions in the Selective Catalytic Reduction (SCRs) process. In this work the production and the role of the increased NO₂ concentration in the Ag/Al₂O₃ catalyst for the SCR process of NO_x removal at low exhaust gas temperatures under real engine operation has been investigated. We have increased the NO₂ concentration available for the SCR process with i) the addition of different NH₃ and H₂ mixtures upstream the SCR catalyst and/or ii) by the use of a Pt based Diesel Oxidation Catalyst (DOC) in front of the Ag/Al₂O₃ catalyst, leading in promoting the "Fast – SCR" like reaction by utilising the available NH₃ mainly at low reaction temperature. The incorporation of the DOC in front of the Ag/Al₂O₃ showed the same effect as it enhanced the NO₂ availability for the SCR process.

Key works:

Hydrogen, Fast - SCR, NOx reduction, NO2, Emissions, IC engines

1. Introduction

Several technologies including advanced fuel injection strategies, variable valve timing (VVT), exhaust gas recirculation (EGR), etc. have been developed for the control of NO_x emissions in diesel engine technology [1, 2]. Research has also been focused in the design of novel catalytic aftertreatment systems such as the selective catalytic reduction (SCR) of NO_x by NH₃ in lean burn conditions using vanadium [3] and manganese [4] based catalysts and Cu [5, 6] or Fe – containing zeolites [7-9], (Eq. 1 – 3) [3]. In addition to NH₃ – SCR, other researches have reported that silver coated alumina, i.e. Ag/Al₂O₃ is a promising catalyst in lean NOx reduction through the use of hydrocarbons (Eq. 4). The low activity of this catalyst at actual exhaust diesel temperature conditions can be promoted by the presence of H₂ [10]. Even more, recent studies also demonstrated successful NH₃ – SCR on the Ag/Al₂O₃ catalyst in addition to HC-SCR, as long as the reaction is assisted by H₂ [11, 12]. The H₂ promoted NH₃ - SCR on Ag/Al₂O₃ can start at comparatively lower temperature and achieve high NOx conversion [13, 14]. NO/NH₃ – SCR (standard SCR): $4NH_3 + 4NO + O_2 \rightarrow 4N_2 + 6H_2O$ (1)

$$NO_2/NH_3 - SCR: 8NH_3 + 6NO_2 \rightarrow 7N_2 + 12H_2O$$

$$NO/NO_2/NH_3 - SCR (Fast SCR): 2NH_3 + NO + NO_2 \rightarrow 2N_2 + 3H_2O$$
(3)

$$\mathrm{HC} - \mathrm{SCR:} \, \mathrm{C}_{\mathrm{n}}\mathrm{H}_{\mathrm{m}}(\mathrm{g}) + \left(2\mathrm{n} + \frac{\mathrm{m}}{2}\right)\mathrm{NO}(\mathrm{g}) \rightarrow \left(\mathrm{n} + \frac{\mathrm{m}}{4}\right)\mathrm{N}_{2}(\mathrm{g}) + \mathrm{nCO}_{2}(\mathrm{g}) + \left(\frac{\mathrm{m}}{2}\right)\mathrm{H}_{2}\mathrm{O}(\mathrm{g}) \tag{4}$$

In the literature, the role of H₂ in HC – SCR is attributed to the formation of Ag clusters (Ag_n^{δ^+}) on Ag/Al₂O₃ via H₂ reduction of Ag⁺ ions [15]. It was proposed that the formed Ag clusters work with H⁺ ions in reducing O₂ to yield superoxide O₂⁻, which is known as the key intermediate for the activation of radical reactions involving both hydrocarbon and NO species that finally leads to N₂ production. Other reaction pathways proposed intermediates species formation such as amines and ammonia that promote the HC – SCR [16, 17]. There are suggestions that NH₃ – SCR is actually part of HC – SCR on the silver catalyst. Hydrogen assisted NH₃ – SCR might also promotes the Fast – SCR reaction (Eq. 3); through the production of NO₂ [18]. The catalytic production of NO₂ that commonly applied is NO oxidation to NO₂, which is kinetically limited at low temperatures and thermodynamically limited at high temperatures. In any case higher temperatures than those existing in diesel engine exhausts are required resulting in fuel economy and CO₂ emissions penalties.

The current research is largely motivated by the above proposed mechanisms and limitations, focusing on investigating novel catalytic alternatives to increase the NO₂ availability without increasing the global carbon footprint of the process and its effect on the NH_3 – SCR reaction over the Ag/Al₂O₃ catalyst. The approaches can be described as i) hydrogen addition directly to the SCR, ii) Pt/Al₂O₃ - DOC placement in the front of the SCR and iii) hydrogen addition upstream the DOC and the SCR [19-21]. The well know storage limitations of hydrogen for automotive applications could be solved through the carbon free process of on-board catalytically production of hydrogen through ammonia exhaust gas reforming.

2. Experimental procedure

Silver SCR catalyst (Ag/Al₂O₃): The HC – SCR catalyst used was provided by Johnson Matthey; a 2 wt. % Ag/Al₂O₃ catalyst prepared by impregnating γ – alumina (surface area ~150 m²/g) with aqueous AgNO₃ before drying and calcining in air for 2 h at 500 °C. The catalyst was made into an aqueous suspension, which was then uniformly coated onto ceramic monolith substrates (diameter 1 inch, length 3 inches) with 600 cpsi cell density.

DOC catalyst (Pt/Al₂O₃): The Pt based DOC catalyst was prepared by impregnation, and then coated at a low loading onto a cordierite honeycomb monolith substrate with diameter of 115 mm and length 75 mm and with high cell density (600 cpsi).

Engine conditions and exhaust gas composition: In the current study, the engine was operated at various load conditions producing exhaust gas with range of emission NOx, THC, CO and etc. concentrations (Table 1).

Test rig configuration: The test rig is illustrated in Fig. 1 exhaust gas in the SCR reactor was controlled with the mean of a flow meter and the reactor temperature is controlled by the mean of a furnace. In the test with DOC, the catalyst was loaded into the exhaust manifold. Temperatures were measurements in several points including both before and after the catalysts and in several places along the engine exhaust pipe. H₂ was injected before and after the DOC while NH₃ was introduced only after the DOC (upstream the silver catalyst) for the purpose of NH₃ – SCR. The

hydrogen concentration in the exhaust was selected based on values that can be achieved using fuel reforming [22, 23] and was measured using a Hewlett Packard 5890 II gas chromatograph (GC) with thermal conductivity detector (TCD) using argon as carrier gas. Whereas, NH₃ and other exhaust species (e.g. NOx, THC and etc.) were recorded by a MKS MultiGAS 2030 FTIR analyser (Fourier Transform Infrared Spectroscopy) (Fig. 1). An IR detector was used to confirm some of the FTIR measurements and provide an additional reading of the exhaust O₂.

Experimental procedures: The study was first carried out using different H_2 additions onto the DOC and SCR catalysts. Each of the catalysts was investigated in isolation. Their individual performances under changing exhaust gas components were assessed at various engine loads. Due to the existence of the engine produced NO₂ (Table 1), the NO to NO₂ conversion and the overall NO₂/NO ratio at the DOC outlet were calculated separately by Eq. 5 and 6.

NO to NO₂ Conversion =
$$\frac{NO_2 A fter DOC - NO_2 Before DOC}{NO_{Before DOC}} \times 100 \%$$
(5)
NO₂/NO Ratio =
$$\frac{NO_2 A fter DOC}{NO_A fter DOC}$$
(6)

Then the DOC and SCR catalysts were placed together (DOC in the front) in the engine exhaust in a combined form. Different levels of H₂ were introduced to study their performance in producing NO₂ or promoting the NH₃ - SCR through the enhanced NO₂ production. Since the DOC was not placed inside a furnace but directly into the exhaust manifold, its temperature was dependant on the engine exhaust temperature at each load. On the other hand, the temperature of the SCR catalyst was controlled by means of furnace for either constant temperature or temperature ramp up experiments. Under ramp up tests, the SCR reactor temperature was increased at 10 °C per every 2 minutes, giving a reaction region from 150 to 500 °C, whereas the SCR temperature in the constant temperature tests was kept constant for at least 20 minutes. Some of the SCR catalyst temperatures were chosen to match the actual exhaust gas temperatures while in some other cases were different. This was done to understand the influence of temperature under constant exhaust gas composition. This could well be the case with the different engine technologies. Depending on the specific engine load, NH₃ was delivered at equal molar ratio to the engine NOX (NH₃:NOX = 1.0) for all SCR reactions, unless stated otherwise. The total use of H₂, either on the individual catalyst or in the combined system, did not exceed 8000 ppm. The engine speed at 1500 rpm resulted in a GHSV of approximately 35000 h⁻¹ over the DOC catalyst. This value was kept throughout the study. The same GHSV was also applied to the Ag/Al₂O₃ catalyst. For convenience, all the test conditions are summarised in Table 2.

3. Results and Discussion

3.1 NO to NO₂ conversion with H₂ addition in the DOC (Pt/Al₂O₃)

The effects of H_2 on the Pt/Al₂O₃ catalyst outlet temperature, exhaust hydrocarbon (HC) and NO to NO₂ conversion are shown in Fig. 2. In addition, the calculated NO to NO₂ conversion based on the reaction's equilibrium (STANJAN v2.09) is also presented (Figure 2) for a comparison of how the thermodynamic equilibria are affected.

Expressed by Fig. 2a, increasing the hydrogen concentration, raised the catalyst outlet temperature being the rate of increase similar at every H_2 level for all the engine conditions. The exhaust gas analysis downstream the catalyst indicated that all the H_2 was consumed over the catalyst. The observed increase of the catalyst temperature due to exothermic reaction of H_2 might be seen as the major reason for the improvements in the oxidation of CO and HCs. At

low exhaust gas temperatures (i.e. low engine load of 2 Bar IMEP), H_2 addition of 6000 ppm increased the DOC outlet temperature from 180 °C to 230 °C. As indicated in the same figure, this temperature is identical to the temperature reached under the higher engine load of 3 Bar IMEP without H_2 addition. However, in Fig. 2b a difference of nearly 20 % in HC conversion was found between these two conditions, showing that the hydrogen effect on the oxidation reaction is not just a result of the improved catalyst local temperature.

The H_2 effect on NO₂ promotion was shown to be more effective at lower engine exhaust temperatures where thermodynamic equilibrium is reached and the reaction is kinetically limited. On the other hand, the experimentally observed NO₂ concentration started to decrease after the catalyst temperature reached 300 °C and above, as it was also experimentally obtained in studies [24-26] using NO oxidation catalyst. It is shown in the equilibrium calculations the NO to NO₂ oxidation is thermodynamically equilibrium limited at higher temperatures, which is also coincident with the calculations showed in the literatures [24-26].Therefore hydrogen becomes less efficient, when the reaction reaches its thermodynamic limits.

These results suggest that in addition of the exothermic effect of hydrogen, the presence of hydrogen can increase the formation of intermediate species (e.g. OH and HO₂ radicals) [27] that further promote the low temperature CO and HCs oxidation as well as NO to NO₂ conversion. Most importantly the active sites adsorption competition and interaction between the different pollutants should be taken into account as it has been shown that NO₂ participates in the reactions involving C-containing species oxidation at low temperatures [28-30]. Therefore, the reduced levels of CO and HCs facilitated the NO adsorption on the active sites [31] and the lower NO₂ consumption to oxidise HCs and CO thus improved NO₂ net production over the catalyst.

3.2 NO to NO₂ conversion with H₂ addition in the Ag/Al₂O₃ for NH3 – SCR reaction

Hydrogen addition onto Ag/Al_2O_3 with engine exhaust containing 730 ppm of NO_x (high engine load of 4 Bar IMEP) with no NH₃ addition enhanced the NO to NO₂ conversion under the transient condition (Fig 3a). However, it seems that this NO₂ is not reacted within the SCR catalyst which produced NO₂ slippage downstream the catalyst (result in agreement with Azis et al., [32]). In addition to enhanced NO conversion the H₂ also promoted the activation of HCs in the SCR, as seen by the increased CO concentration detected downstream the catalyst (Fig. 3b).

However, as it has been calculated in the previous section the NO to NO₂ reaction is thermodynamically limited at high temperature (Fig. 2c), which explains the decrease in the NO₂ production within the SCR when the temperature was increased as in the case of the DOC. This outcome was in agreement with a recent kinetic modelling [32, 33] and an experimental study [34] where the combined effect of hydrogen and alternative reductants over a Ag/Al₂O₃ catalyst were studied. The "H₂ effect" here was primarily attributed to form new Ag active sites and the decomposition of self - inhibiting surface nitrate species, which were formed due to the presence of NO and NO₂ (e.g. precursors of the nitrate species) and strongly adsorbed onto the catalyst's active site. As can be inferred from Fig. 3a, this blocking effect on the catalyst was not sufficiently removed at low catalyst temperature (< 180 °C) being obvious the kinetic limitation. However, when a H₂ addition of 2000 ppm was applied the accessibility to the catalytic active sites was provided and the NO₂ production was increased according to the reaction equilibrium.

When NH_3 was co – fed into the engine exhaust with a constant H_2 addition (Fig. 4a), increasing its concentration caused the total amount of NO_2 downstream the catalyst to decrease. This indicates that the produced NO_2

was immediately consumed reducing NOx to N₂ (see Eq. 1 - 3). On the other hand, removing H₂ resulted in no NO_x conversion; while significant NH₃ conversion due to oxidation could only be observed when the catalyst temperature was above 380 °C (results not shown). Hence, all these observations suggest that hydrogen has the role of a co – reductant that is also promoting the function of the rest of the reductants (in this case NH₃) in the SCR mechanism. Furthermore, the NO₂ slippage downstream the catalyst coincide with the depletion of the added NH₃ at around the same temperature (Fig. 4a and b). This suggests that with the primary reactant NH₃ being gradually increased, the formed NO₂ was involved in the de-NOx reactions significantly which decreased the NO₂ found downstream the SCR catalyst. Compared to the NH₃ conversions at lower NH₃ additions (Fig. 4b), the lack of NO₂ within this temperature region might restrict the SCR activity when the NH₃:NO_x ratio was getting closer to the equal molar ratio. Therefore, increased NO₂ concentration would be inferred as beneficial to the NO_x conversion under this temperature condition.

In addition to the above experiments, the transient condition was also applied to the combined system (DOC+SCR) with the same exhaust composition (without NH_3) and 8000 ppm of H_2 over the SCR catalyst, to investigate whether any exhaust component (i.e. unburned HC) could contribute to the NOx conversion within the studied temperature range of 140 - 440 °C. The results showed negligible NOx conversion across the temperature ramp (Fig. A1, appendix).

3.3 SCR activity at low reaction temperature (< 200 °C) with increased NO₂ concentration

For the combined system at 230°C exhaust temperature (engine load 3 Bar IMEP), a NO₂/NO ratio of ~ 0.5 was maintained at the DOC outlet, therefore no H₂ promotion was needed over the DOC (as shown in Fig. 2c).

Increasing the SCR's inlet NO₂ concentration at the lowest temperature of 150 °C improved the overall NOx conversion (Fig. 5a). As shown by Fig. 5b, the utilisation of the NO₂ was improved over the SCR catalyst at increased hydrogen levels but noticeable amounts of unconverted NO₂ were still recorded after the catalyst. The theoretical NOx conversion can be estimated assuming stoichiometric Fast – SCR (Eq. 3) as the only reaction occurring over the SCR catalyst using the amount of NO₂ and NO available at the SCR catalyst inlet: i) the engine – out NOx (listed in Table 1) and ii) the NO₂/NO ratio after the DOC (Fig. 2c). Figure 5c shows that at those low temperatures the reacted NO and NO₂ were lower than the stoichiometry predicted by the Fast-SCR reaction. It was also obtained that the total NOx conversion was contributed primarily by the reduction of NO₂, whereas the reduction in NO was shown to be much lower. In a recent study, Ciardelli et al. showed that the ammonium nitrate (NH₄NO₃) was an essential intermediate in the Fast – SCR mechanism (please see equations 7 and 8 below) [35]. However, when the temperature is below 170 °C, the formed NH₄NO₃ will rapidly deposit on the catalyst inhibiting NO and NO₂ conversions as such experimentally observed in Fig 5c.

$$2NO_2 + 2NH_3 \to NH_4NO_3 + N_2 + H_2O \tag{7}$$

$$NH_4NO_3 + NO \rightarrow N_2 + NO_2 + 2H_2O$$
 (8)

Nevertheless, when the catalyst temperature was increased from 150 °C to 180 °C, no significant NO₂ (< 5 ppm) was detected while the SCR catalyst was fed with the exhaust produced at low engine load (i.e. 2 Bar IMEP) and the DOC's NO₂ production was limited. When H₂ was added to enhance the DOC's contribution in NO to NO₂ conversion (as seen in section 3.1) the NO_x conversion within the SCR was improved compared to when hydrogen was only added

upstream the SCR (Fig. 6a). Shown by Fig. 6b, when the lowest amount of H_2 i.e. 2000 ppm was maintained over the SCR catalyst, the actual NOx conversion followed closely the stoichiometric prediction at every inlet NO₂ concentration. This indicates the NOx conversion was predominantly a result of the "Fast – SCR" like process not being inhibiting by the solid nitrates. As the H_2 addition in the SCR was increased from 2000 ppm to 4000 ppm, (for the different NO₂/NO studied ratios) the catalyst activity in reducing NO_x emissions was further improved (Fig. 6b). This implies that while the incorporation of DOC improved the SCR activity by providing fixed amounts of NO₂, the SCR catalyst itself became more active in reducing NO_x due to further increase of NO₂ availability when H₂ addition was increased (Fig 6a and 6b).

Hence, the better SCR performance implies that the Ag/Al_2O_3 catalyst NH_3 – SCR performance in reducing NO_x emissions in a real engine exhaust it is largely determined by the system's NO_2 availability. The NO_2 importance might not be as evidenced in a laboratory conditions where the particular SCR catalyst performance evaluated with the use of simulated gases (non-real exhaust) and in the absent of solid state emissions. As we have previously reported (e.g. [36]) the presence of both unburned diesel fuel and solid particles in the engine exhaust can lead to the Ag/Al_2O_3 catalyst deactivation through partially blocked catalyst pores. This leads to increased diffusion resistance and thus a decrease in the activation energy. Therefore, the oxidation of NO (to NO_2) it is an important step not only within the overall SCR reaction, but under real world conditions, the increased NO_2 can react with the C-containing species on catalyst surface and enhance the pore diffusion rates.

3.4 SCR activity at high reaction temperature with increased NO₂ concentration

Shown by Fig 7a and the comparison between Fig 6a and Fig 7b, the increased catalyst temperature improved the SCR reaction conversion but diminished the NO₂ promotional effect (i.e. the benefit to increase the NO₂/NO ratio upstream the SCR) on the overall NOx conversion. The actual converted NOx and the "Fast – SCR" prediction using the inlet NO₂ are plotted in Fig. 7c for exhaust gas from the 3 Bar IMEP engine condition. The improved in NOx conversion (higher than the predicted conversely to low exhaust temperature conditions) may also indicate the "Fast – SCR" like mechanism was not the only reaction.

At those higher temperatures, the standard SCR reaction (Eq. 1) could be activated [37, 38], thus this would allow the NOx conversion to improve at increased temperature regardless of the system's NO₂ concentration: as indicated in Fig. 7c and 7d. When the temperature was greater than 275 °C, the NO₂/NH₃ – SCR (Eq. 2) reaction could equally happen [35], but this requires more NH₃ than the "Fast – SCR" to convert the same amount of NO_x, i.e. NO₂ (Eq. 2 vs. Eq. 3). Thus, an increase in the inlet NO₂ concentration would not significantly promote NOx conversion, impairing the NO₂'s promotional effect at higher reaction temperature. In addition, at increased temperature (> 230 °C) and provided the DOC is not in use, the HCs could still contribute to some of the NOx conversion. Supported by the above reasons, the use of DOC at high exhaust temperature (e.g. 4 Bar IMEP) was shown to be only necessary at low SCR reaction temperature, Fig. 7d.

Figure 8 shows the unconverted ammonia downstream the SCR catalyst. All these results are acquired from the 2 Bar IMEP condition. The unconverted NH₃, or referred as the "ammonia slippage", is consistent with the NOx conversion shown in Fig. 6a and Fig. 7c, confirming the increased NO₂ concentration was generally more beneficial to the low temperature NOx removal. Due to the human and environmental hazard effects of NO₂ as well as the toxicity ofNH₃, it is necessary to suppress their emission to the atmosphere to very low levels. Results here indicate, the NO₂ promoted NH₃ – SCR did not just improved the reaction's low temperature activity, it also achieved efficient removal of

ammonia slippage (< 20 ppm) at comparatively lower H_2 promotion. Further optimisation, which is out of the scope of this research work, could be preform to determine the optimal NH_3 dosing depending on the species concentration and as it has been investigated in [39] in the case of only NH_3 -SCR.

4. Conclusion

Different alternatives for the increase of the NO₂ availability without increasing fuel economy and the global carbon footprint of the process as well as its effect in the activity of $NH_3 - SCR$ were investigated in NOx reduction over an Ag/Al₂O₃ catalyst using actual diesel engine lean exhaust gas in real engine operation.

NO conversion to NO₂ was obtained over the Ag/Al₂O₃ with an oxidative promotion from H₂. The formed NO₂ was suggested to be used in the SCR reaction immediately after its production and with the added NH₃. This allowed a "Fast – SCR" like process, whose activity at low reaction temperature was shown to be largely determined by the system's NO₂ availability. The use of a Pt/Al₂O₃ based DOC in increasing the exhaust NO₂ level was also shown to improve significantly the SCR performance, which indicates the DOC simulated or even performed better the function of H₂ over the SCR catalyst. Hence one of the H₂ roles in real engine applications is confirmed to be a promoter of the NO oxidation and to affect the overall SCR performance at low reaction temperature i.e. around 200 °C or less in this case. However, this promotional effect of increased NO₂ concentration upstream the SCR catalyst was shown to be diminished by the increased reaction temperature, thus the SCR reaction's H₂ dependence was reduced as well.

In general, the results suggest increasing the NO₂ concentration, either in the engine exhaust by means of combustion or from other catalytic aftertreatment and/or the Ag/Al₂O₃ itself, can improve significantly the H_2 – assisted NH₃ – SCR in low temperature NO_x control and at the same time reduce the system's demand on H₂ level. The approaches considered here are based on the use of hydrogen as a promoter which could be obtained through on-board ammonia exhaust gas reforming using the waste heat of the exhaust. Therefore, those approaches do not require the use of external hydrocarbons which will result in considerable higher fuel economy and CO₂ emissions penalties.

The findings of this research work could provide key information for kinetic studies which could also include those reactions under the presence of NH_3 and hydrogen in Ag/Al_2O_3 catalyst. Furthermore, they can also be used for further optimisation, to determine the optimal hydrogen and NH_3 dosing depending on the actual exhaust species concentration, temperature and exhaust flow enabling high de-NOx activity while limiting any NH_3 and NO_2 slippage downstream the catalyst which could be released to the atmosphere.

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Figure 1: Experimental setup.

Figure 2: Effect of hydrogen addition over the DOC on (a) outlet temperature; (b) HC conversion and (c) NO to NO₂ conversion.

Figure 3: Emission concentration after the SCR catalyst under various H₂ additions without NH₃ (a) NO₂ and (b) CO.

Figure 4: Emission concentration after the SCR under various NH_3 additions with a fixed H_2 addition (a) NO_2 and (b) NH_3 .

Figure 5: Effect of hydrogen addition at 3 Bar IMEP, (a) NOx reduction with and without the increased NO_2 concentration (b) NO_2 consumed over the SCR and (c) experimentally and calculated (based on Fast – SCR stoichiometry) NOx conversion.

Figure 6: Effect of hydrogen on NOx conversion at 2 Bar IMEP at SCR catalyst inlet temperature of 180 $^{\circ}$ C (a) 2000, 4000 and 8000 ppm H₂ addition upstream SCR and (b) experimental and calculated (based on Fast – SCR stoichiometry) NOx conversion at 2000 and 4000 ppm H₂ addition.

Figure 7: NOx conversions at (a) 3 Bar IMEP and (b) 2 Bar IMEP; (c) 3 Bar IMEP (experimental and calculated based on Fast – SCR stoichiometry) and (d) 4 Bar IMEP.

Figure 8: NH₃ detected after the SCR catalyst at 2 Bar IMEP.

- Table 1: Engine conditions and average emissions.
- Table 2: Summarise of conditions in each experimental run.



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Figure 7: NOx conversions in the SCR at different engine loads (a) 3 Bar IMEP and (b) 2 Bar IMEP; (c) 3 Bar IMEP (experimental and calculated based on Fast – SCR stoichiometry) and (d) 4 Bar IMEP.



Figure 8: NH₃ slippage after the SCR catalyst at 2 Bar IMEP.

Table 1: Engine conditions and average emissions.

Engine Load (Nm)	IMEP*	NO	NO ₂	THC**	СО	CO ₂	O ₂	H ₂ O
	(bar)	(ppm)	(ppm)	(ppm)	(ppm)	(%)	(%)	(%)
8	2	320	30	415	160	2.53	15.6	2.54
16	3	495	40	420	120	3.71	15.1	3.47
24	4	690	40	435	110	6.11	14.9	4.45

* IMEP: indicated mean effective pressure

**THC: total hydrocarbon based on C₁ emission

Table 2: Summarise of conditions in each experimental run.

Type of run	Cat. used	Engine load (bar IMEP)	DOC Temp. (°C)	SCR Temp. (°C)	H ₂ on DOC (ppm)	H ₂ on SCR (ppm)	NH ₃ on SCR (ppm)
Steady - state	DOC alone	2	180 (exhaust)			NA	NA
		3	230 (exhaust)	NA	0, 1000, 2000, 3000, 4000, 6000		
		4	300 (exhaust)				
Transient	SCR alone	4	NA	150 – 500 (ramp)	NA	8000	0, 200, 350, 550
Steady - state	DOC + SCR	2	180 (exhaust)	180* (furnace)	0.2000.4000	2000, 4000, 8000	350 (match exhaust
				230 (furnace)	0, 2000, 4000		NOx)
		3	230 (exhaust)	150 (furnace)		2000, 4000, 8000	530 (match exhaust NOx)
				200 (furnace)	0		
				230* (furnace)			
		4	300 (exhaust)	150 (furnace)		8000	730 (match exhaust NOx)
				200 (furnace)	0		
				250 (furnace)	0		
				300* (furnace)			
Transient		4	300 (exhaust)	150 – 500 (ramp)	0	8000	0

* SCR inlet temperature matched the exhaust temperature

Appendix



Figure A1: NOx and exhaust HC conversions over the temperature ramp with and without the DOC being placed in front of the SCR catalyst