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Increased NO\textsubscript{2} Concentration in the Diesel Engine Exhaust for Improved Ag/Al\textsubscript{2}O\textsubscript{3} Catalyst NH\textsubscript{3}-SCR activity

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Abstract

Increasing the NO\textsubscript{2} availability in some aftertreatment systems enhance their performance in reducing pollutants from internal combustion (IC) engines but result in significant fuel economy and CO\textsubscript{2} emissions penalties. The presence of NO\textsubscript{2} 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 NO\textsubscript{2} concentration in the Ag/Al\textsubscript{2}O\textsubscript{3} catalyst for the SCR process of NO\textsubscript{x} removal at low exhaust gas temperatures under real engine operation has been investigated. We have increased the NO\textsubscript{2} concentration available for the SCR process with i) the addition of different NH\textsubscript{3} and H\textsubscript{2} mixtures upstream the SCR catalyst and/or ii) by the use of a Pt based Diesel Oxidation Catalyst (DOC) in front of the Ag/Al\textsubscript{2}O\textsubscript{3} - SCR catalyst. In the case of NH\textsubscript{3} and H\textsubscript{2} mixtures additions, H\textsubscript{2} enhances the NO\textsubscript{2} production on the Ag/Al\textsubscript{2}O\textsubscript{3} catalyst, leading in promoting the “Fast – SCR” like reaction by utilising the available NH\textsubscript{3} mainly at low reaction temperature. The incorporation of the DOC in front of the Ag/Al\textsubscript{2}O\textsubscript{3} showed the same effect as it enhanced the NO\textsubscript{2} availability for the SCR process.

Key works:

Hydrogen, Fast – SCR, NO\textsubscript{x} reduction, NO\textsubscript{2}, 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\textsubscript{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\textsubscript{x} by NH\textsubscript{3} 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 NH\textsubscript{3} – SCR, other researches have reported that silver coated alumina, i.e. Ag/Al\textsubscript{2}O\textsubscript{3} is a promising catalyst in lean NO\textsubscript{x} 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 H\textsubscript{2} [10]. Even more, recent studies also demonstrated successful NH\textsubscript{3} – SCR on the Ag/Al\textsubscript{2}O\textsubscript{3} catalyst in addition to HC-SCR, as long as the reaction is assisted by H\textsubscript{2} [11, 12]. The H\textsubscript{2} promoted NH\textsubscript{3} - SCR on Ag/Al\textsubscript{2}O\textsubscript{3} can start at comparatively lower temperature and achieve high NO\textsubscript{x} conversion [13, 14].

\text{NO/NH\textsubscript{3} – SCR (standard SCR): } 4\text{NH}_3 + 4\text{NO} + \text{O}_2 \rightarrow 4\text{N}_2 + 6\text{H}_2\text{O} \quad (1)
NO₂/NH₃ – SCR: 8NH₃ + 6NO₂ → 7N₂ + 12H₂O  
(2)

NO/NO₂/NH₃ – SCR (Fast SCR): 2NH₃ + NO + NO₂ → 2N₂ + 3H₂O  
(3)

HC – SCR: \( c_nH_m(g) + \left( 2n + \frac{m}{2} \right) NO(g) \rightarrow \left( n + \frac{m}{7} \right) N_2(g) + nCO_2(g) + \left( \frac{m}{7} \right) H_2O(g) \)  
(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 O\(_2\) to yield superoxide O\(_2^−\), 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 NH₃ – 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, NH\textsubscript{3} and other exhaust species (e.g. NO\textsubscript{x}, 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 O\textsubscript{2}.

Experimental procedures: The study was first carried out using different H\textsubscript{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 NO\textsubscript{2} (Table 1), the NO to NO\textsubscript{2} conversion and the overall NO\textsubscript{2}/NO ratio at the DOC outlet were calculated separately by Eq. 5 and 6.

\[
\text{NO to NO}_2\text{ Conversion} = \frac{\text{NO}_2\text{ After DOC} - \text{NO}_2\text{ Before DOC}}{\text{NO} \text{ Before DOC}} \times 100\% \tag{5}
\]

\[
\text{NO}_2/\text{NO} \text{ Ratio} = \frac{\text{NO}_2\text{ After DOC}}{\text{NO} \text{ After DOC}} \tag{6}
\]

Then the DOC and SCR catalysts were placed together (DOC in the front) in the engine exhaust in a combined form. Different levels of H\textsubscript{2} were introduced to study their performance in producing NO\textsubscript{2} or promoting the NH\textsubscript{3} - SCR through the enhanced NO\textsubscript{2} 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, NH\textsubscript{3} was delivered at equal molar ratio to the engine NO\textsubscript{x} (NH\textsubscript{3}:NO\textsubscript{x} = 1.0) for all SCR reactions, unless stated otherwise. The total use of H\textsubscript{2}, 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\textsuperscript{-1} over the DOC catalyst. This value was kept throughout the study. The same GHSV was also applied to the Ag/Al\textsubscript{2}O\textsubscript{3} catalyst. For convenience, all the test conditions are summarised in Table 2.

3. Results and Discussion

3.1 NO to NO\textsubscript{2} conversion with H\textsubscript{2} addition in the DOC (Pt/Al\textsubscript{2}O\textsubscript{3})

The effects of H\textsubscript{2} on the Pt/Al\textsubscript{2}O\textsubscript{3} catalyst outlet temperature, exhaust hydrocarbon (HC) and NO to NO\textsubscript{2} conversion are shown in Fig. 2. In addition, the calculated NO to NO\textsubscript{2} 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\textsubscript{2} level for all the engine conditions. The exhaust gas analysis downstream the catalyst indicated that all the H\textsubscript{2} was consumed over the catalyst. The observed increase of the catalyst temperature due to exothermic reaction of H\textsubscript{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), H₂ 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 H₂ 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 H₂ 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/Al₂O₃ with engine exhaust containing 730 ppm of NOₓ (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 NH₃ was co-fed into the engine exhaust with a constant H₂ addition (Fig. 4a), increasing its concentration caused the total amount of NO₂ downstream the catalyst to decrease. This indicates that the produced NO₂
was immediately consumed reducing NOx to N2 (see Eq. 1 – 3). On the other hand, removing H2 resulted in no NOx 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:NOx ratio was getting closer to the equal molar ratio. Therefore, increased NO2 concentration would be inferred as beneficial to the NOx 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 NH3) and 8000 ppm of H2 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.

\[
2NO_2 + 2NH_3 \rightarrow NH_4NO_3 + N_2 + H_2O \tag{7}
\]

\[
NH_4NO_3 + NO \rightarrow N_2 + NO_2 + 2H_2O \tag{8}
\]

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 NOx 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 \( \text{H}_2 \) i.e. 2000 ppm was maintained over the SCR catalyst, the actual NOx conversion followed closely the stoichiometric prediction at every inlet NO\(_2\) 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 \( \text{H}_2 \) addition in the SCR was increased from 2000 ppm to 4000 ppm, (for the different NO\(_2\)/NO studied ratios) the catalyst activity in reducing NOx emissions was further improved (Fig. 6b). This implies that while the incorporation of DOC improved the SCR activity by providing fixed amounts of NO\(_2\), the SCR catalyst itself became more active in reducing NO\(_x\) due to further increase of NO\(_2\) availability when \( \text{H}_2 \) addition was increased (Fig 6a and 6b).

Hence, the better SCR performance implies that the Ag/Al\(_2\)O\(_3\) catalyst NH\(_3\) – SCR performance in reducing NOx emissions in a real engine exhaust it 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\(_2\)O\(_3\) 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 NO\(_2\) 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 NO\(_2\) promotional effect (i.e. the benefit to increase the NO\(_2\)/NO ratio upstream the SCR) on the overall NOx conversion. The actual converted NOx and the “Fast – SCR” prediction using the inlet NO\(_2\) 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 NO\(_2\) concentration: as indicated in Fig. 7c and 7d. When the temperature was greater than 275 °C, the NO\(_2\)/NH\(_3\) – SCR (Eq. 2) reaction could equally happen [35], but this requires more NH\(_3\) than the “Fast – SCR” to convert the same amount of NO\(_x\), i.e. NO\(_2\) (Eq. 2 vs. Eq. 3). Thus, an increase in the inlet NO\(_2\) concentration would not significantly promote NOx conversion, impairing the NO\(_2\)’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 NH\(_3\), or referred as the “ammonia slippage”, is consistent with the NOx conversion shown in Fig. 6a and Fig. 7c, confirming the increased NO\(_2\) concentration was generally more beneficial to the low temperature NOx removal. Due to the human and environmental hazard effects of NO\(_2\) as well as the toxicity ofNH\(_3\), it is necessary to suppress their emission to the atmosphere to very low levels. Results here indicate, the NO\(_2\) promoted NH\(_3\) – 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\textsubscript{2} promotion. Further optimisation, which is out of the scope of this research work, could be performed to determine the optimal NH\textsubscript{3} dosing depending on the species concentration and as it has been investigated in [39] in the case of only NH\textsubscript{3}-SCR.

4. Conclusion

Different alternatives for the increase of the NO\textsubscript{2} availability without increasing fuel economy and the global carbon footprint of the process as well as its effect in the activity of NH\textsubscript{3} – SCR were investigated in NO\textsubscript{x} reduction over an Ag/Al\textsubscript{2}O\textsubscript{3} catalyst using actual diesel engine lean exhaust gas in real engine operation.

NO conversion to NO\textsubscript{2} was obtained over the Ag/Al\textsubscript{2}O\textsubscript{3} with an oxidative promotion from H\textsubscript{2}. The formed NO\textsubscript{2} was suggested to be used in the SCR reaction immediately after its production and with the added NH\textsubscript{3}. This allowed a “Fast – SCR” like process, whose activity at low reaction temperature was shown to be largely determined by the system’s NO\textsubscript{2} availability. The use of a Pt/Al\textsubscript{2}O\textsubscript{3} based DOC in increasing the exhaust NO\textsubscript{2} level was also shown to improve significantly the SCR performance, which indicates the DOC simulated or even performed better the function of H\textsubscript{2} over the SCR catalyst. Hence one of the H\textsubscript{2} 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 NO\textsubscript{2} concentration upstream the SCR catalyst was shown to be diminished by the increased reaction temperature, thus the SCR reaction’s H\textsubscript{2} dependence was reduced as well.

In general, the results suggest increasing the NO\textsubscript{2} concentration, either in the engine exhaust by means of combustion or from other catalytic aftertreatment and/or the Ag/Al\textsubscript{2}O\textsubscript{3} itself, can improve significantly the H\textsubscript{2} – assisted NH\textsubscript{3} – SCR in low temperature NO\textsubscript{x} control and at the same time reduce the system’s demand on H\textsubscript{2} 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 CO\textsubscript{2} 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\textsubscript{3} and hydrogen in Ag/Al\textsubscript{2}O\textsubscript{3} catalyst. Furthermore, they can also be used for further optimisation, to determine the optimal hydrogen and NH\textsubscript{3} dosing depending on the actual exhaust species concentration, temperature and exhaust flow enabling high de-NO\textsubscript{x} activity while limiting any NH\textsubscript{3} and NO\textsubscript{2} slippage downstream the catalyst which could be released to the atmosphere.

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Figure 5: Effect of hydrogen addition at 3 Bar IMEP. (a) NOx reduction with and without the increased NO2 concentration (b) NO2 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 °C (a) 2000, 4000 and 8000 ppm H$_2$ addition upstream SCR and (b) experimental and calculated (based on Fast – SCR stoichiometry) NOx conversion at 2000 and 4000 ppm H$_2$ addition.
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:** NH$_3$ slippage after the SCR catalyst at 2 Bar IMEP.
Table 1: Engine conditions and average emissions.

<table>
<thead>
<tr>
<th>Engine Load (Nm)</th>
<th>IMEP* (bar)</th>
<th>NO (ppm)</th>
<th>NO₂ (ppm)</th>
<th>THC** (ppm)</th>
<th>CO (ppm)</th>
<th>CO₂ (%)</th>
<th>O₂ (%)</th>
<th>H₂O (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>2</td>
<td>320</td>
<td>30</td>
<td>415</td>
<td>160</td>
<td>2.53</td>
<td>15.6</td>
<td>2.54</td>
</tr>
<tr>
<td>16</td>
<td>3</td>
<td>495</td>
<td>40</td>
<td>420</td>
<td>120</td>
<td>3.71</td>
<td>15.1</td>
<td>3.47</td>
</tr>
<tr>
<td>24</td>
<td>4</td>
<td>690</td>
<td>40</td>
<td>435</td>
<td>110</td>
<td>6.11</td>
<td>14.9</td>
<td>4.45</td>
</tr>
</tbody>
</table>

* IMEP: indicated mean effective pressure  
**THC: total hydrocarbon based on C₁ emission

Table 2: Summarise of conditions in each experimental run.

<table>
<thead>
<tr>
<th>Type of run</th>
<th>Cat. used</th>
<th>Engine load (bar IMEP)</th>
<th>DOC Temp. (°C)</th>
<th>SCR Temp. (°C)</th>
<th>H₂ on DOC (ppm)</th>
<th>H₂ on SCR (ppm)</th>
<th>NH₃ on SCR (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steady - state</td>
<td>DOC alone</td>
<td>2</td>
<td>180 (exhaust)</td>
<td>NA</td>
<td>0, 1000, 2000, 3000, 4000, 6000</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>230 (exhaust)</td>
<td>NA</td>
<td>0, 2000, 4000</td>
<td>2000, 4000, 8000</td>
<td>350 (match exhaust NOx)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>300 (exhaust)</td>
<td>150 – 500 (ramp)</td>
<td>NA</td>
<td>8000</td>
<td>0, 200, 350, 550</td>
</tr>
<tr>
<td>Transient</td>
<td>SCR alone</td>
<td>4</td>
<td>NA</td>
<td>150 – 500 (ramp)</td>
<td>NA</td>
<td>8000</td>
<td>0, 200, 350, 550</td>
</tr>
<tr>
<td>Steady - state</td>
<td>DOC + SCR</td>
<td>2</td>
<td>180 (exhaust)</td>
<td>180* (furnace)</td>
<td>0, 2000, 4000</td>
<td>2000, 4000, 8000</td>
<td>350 (match exhaust NOx)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>3</td>
<td>230 (exhaust)</td>
<td>150 (furnace)</td>
<td>0</td>
<td>2000, 4000, 8000</td>
<td>530 (match exhaust NOx)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4</td>
<td>300 (exhaust)</td>
<td>150 (furnace)</td>
<td>0</td>
<td>8000</td>
<td>730 (match exhaust NOx)</td>
</tr>
<tr>
<td>Transient</td>
<td></td>
<td>4</td>
<td>300 (exhaust)</td>
<td>150 – 500 (ramp)</td>
<td>0</td>
<td>8000</td>
<td>0</td>
</tr>
</tbody>
</table>

* SCR inlet temperature matched the exhaust temperature
Figure A1: NOx and exhaust HC conversions over the temperature ramp with and without the DOC being placed in front of the SCR catalyst.
NOx REDUCTION FROM LOW TEMPERATURE DIESEL EXHAUST

BY ADDING HYDROGEN OVER Ag/Al2O3
INCREASING NO2/NO RATIO

H2

NO

NO2

Ag/Al2O3 CATALYST

+ NH3

(Fast SCR): 2NH3 + NO + NO2 = 2N2 + 3H2O
4NH3 + 4NO + O2 = 4N2 + 6H2O
8NH3 + 6NO2 = 7N2 + 12H2O

LESS H2 AND A DIESEL OXIDATION CATALYST

2NO + O2 = 2NO2

Pt/Al2O3 CATALYST

DIESEL ENGINE COMBUSTION
Highlights

- NO$_2$ formation in Ag/Al$_2$O$_3$ catalyst was found to increase with H$_2$ addition
- Increased NO$_2$ formation on Ag/Al$_2$O$_3$ enhanced its NH$_3$ – SCR activity at low reaction temperature
- NO$_2$ formation prior to Ag/Al$_2$O$_3$ (i.e. engine or DOC) will benefits the NH$_3$ – SCR activity
- The NO$_2$ promotion diminished at high temperature