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

Wang, Wentao; Herreros, Jose M.; Tsolakis, Athanasios; York, Andrew P.e.

DOI:

[10.1016/j.cej.2015.02.067](https://doi.org/10.1016/j.cej.2015.02.067)

License:

Other (please specify with Rights Statement)

Document Version

Peer reviewed version

Citation for published version (Harvard):

Wang, W, Herreros, JM, Tsolakis, A & York, APE 2015, 'Increased NO₂ concentration in the diesel engine exhaust for improved Ag/Al₂O₃ catalyst NH₃-SCR activity', *Chemical Engineering Journal*, vol. 270, pp. 582-589. <https://doi.org/10.1016/j.cej.2015.02.067>

[Link to publication on Research at Birmingham portal](#)

Publisher Rights Statement:

NOTICE: this is the author's version of a work that was accepted for publication. Changes resulting from the publishing process, such as peer review, editing, corrections, structural formatting, and other quality control mechanisms may not be reflected in this document. Changes may have been made to this work since it was submitted for publication. A definitive version was subsequently published as W. Wang, Jose.M. Herreros, A. Tsolakis, A.P.E. York, Increased NO₂ Concentration in the Diesel Engine Exhaust for Improved Ag/Al₂O₃ Catalyst NH₃-SCR activity, *Chemical Engineering Journal* (2015), doi: <http://dx.doi.org/10.1016/j.cej.2015.02.067>

General rights

Unless a licence is specified above, all rights (including copyright and moral rights) in this document are retained by the authors and/or the copyright holders. The express permission of the copyright holder must be obtained for any use of this material other than for purposes permitted by law.

- Users may freely distribute the URL that is used to identify this publication.
- Users may download and/or print one copy of the publication from the University of Birmingham research portal for the purpose of private study or non-commercial research.
- User may use extracts from the document in line with the concept of 'fair dealing' under the Copyright, Designs and Patents Act 1988 (?)
- Users may not further distribute the material nor use it for the purposes of commercial gain.

Where a licence is displayed above, please note the terms and conditions of the licence govern your use of this document.

When citing, please reference the published version.

Take down policy

While the University of Birmingham exercises care and attention in making items available there are rare occasions when an item has been uploaded in error or has been deemed to be commercially or otherwise sensitive.

If you believe that this is the case for this document, please contact UBIRA@lists.bham.ac.uk providing details and we will remove access to the work immediately and investigate.

Accepted Manuscript

Increased NO₂ Concentration in the Diesel Engine Exhaust for Improved Ag/Al₂O₃ Catalyst NH₃-SCR activity

Wentao Wang, Jose.M. Herreros, Athanasios Tsolakis, Andrew P.E. York

PII: S1385-8947(15)00276-4
DOI: <http://dx.doi.org/10.1016/j.cej.2015.02.067>
Reference: CEJ 13320

To appear in: *Chemical Engineering Journal*

Received Date: 3 December 2014
Revised Date: 13 February 2015
Accepted Date: 16 February 2015

Please cite this article as: W. Wang, Jose.M. Herreros, A. Tsolakis, A.P.E. York, Increased NO₂ Concentration in the Diesel Engine Exhaust for Improved Ag/Al₂O₃ Catalyst NH₃-SCR activity, *Chemical Engineering Journal* (2015), doi: <http://dx.doi.org/10.1016/j.cej.2015.02.067>

This is a PDF file of an unedited manuscript that has been accepted for publication. As a service to our customers we are providing this early version of the manuscript. The manuscript will undergo copyediting, typesetting, and review of the resulting proof before it is published in its final form. Please note that during the production process errors may be discovered which could affect the content, and all legal disclaimers that apply to the journal pertain.

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

^a*School of Mechanical Engineering, University of Birmingham, Edgbaston, B15 2TT, UK*

^b*Johnson 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 NO_x 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 - SCR catalyst. In the case of NH₃ and H₂ mixtures additions, H₂ enhances the NO₂ production on 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, NO_x 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 NO_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 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 NO_x conversion [13, 14].

In the literature, the role of H_2 in HC – SCR is attributed to the formation of Ag clusters ($\text{Ag}_n^{\delta+}$) on $\text{Ag}/\text{Al}_2\text{O}_3$ via H_2 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 N_2 production. Other reaction pathways proposed intermediates species formation such as amines and ammonia that promote the HC – SCR [16, 17]. There are suggestions that NH_3 – SCR is actually part of HC – SCR on the silver catalyst. Hydrogen assisted NH_3 – SCR might also promotes the Fast – SCR reaction (Eq. 3); through the production of NO_2 [18]. The catalytic production of NO_2 that commonly applied is NO oxidation to NO_2 , 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 CO_2 emissions penalties.

The current research is largely motivated by the above proposed mechanisms and limitations, focusing on investigating novel catalytic alternatives to increase the NO_2 availability without increasing the global carbon footprint of the process and its effect on the NH_3 – SCR reaction over the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst. The approaches can be described as i) hydrogen addition directly to the SCR, ii) $\text{Pt}/\text{Al}_2\text{O}_3$ - 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 ($\text{Ag}/\text{Al}_2\text{O}_3$): The HC – SCR catalyst used was provided by Johnson Matthey; a 2 wt. % $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst prepared by impregnating γ – alumina (surface area $\sim 150 \text{ m}^2/\text{g}$) with aqueous AgNO_3 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 ($\text{Pt}/\text{Al}_2\text{O}_3$): 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 NO_x , 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. H_2 was injected before and after the DOC while NH_3 was introduced only after the DOC (upstream the silver catalyst) for the purpose of NH_3 – 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_3 and other exhaust species (e.g. NO_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_2 .

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 NO_2 (Table 1), the NO to NO_2 conversion and the overall NO_2/NO ratio at the DOC outlet were calculated separately by Eq. 5 and 6.

$$\text{NO to NO}_2 \text{ Conversion} = \frac{\text{NO}_2 \text{ After DOC} - \text{NO}_2 \text{ Before DOC}}{\text{NO Before DOC}} \times 100 \% \quad (5)$$

$$\text{NO}_2/\text{NO Ratio} = \frac{\text{NO}_2 \text{ After DOC}}{\text{NO After DOC}} \quad (6)$$

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_2 were introduced to study their performance in producing NO_2 or promoting the NH_3 - SCR through the enhanced NO_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_3 was delivered at equal molar ratio to the engine NO_x ($\text{NH}_3:\text{NO}_x = 1.0$) for all SCR reactions, unless stated otherwise. The total use of H_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^{-1} over the DOC catalyst. This value was kept throughout the study. The same GHSV was also applied to the $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst. For convenience, all the test conditions are summarised in Table 2.

3. Results and Discussion

3.1 NO to NO_2 conversion with H_2 addition in the DOC ($\text{Pt}/\text{Al}_2\text{O}_3$)

The effects of H_2 on the $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst outlet temperature, exhaust hydrocarbon (HC) and NO to NO_2 conversion are shown in Fig. 2. In addition, the calculated NO to NO_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_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), 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 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 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 NO_x 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-NO_x 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 NH₃) and 8000 ppm of H₂ over the SCR catalyst, to investigate whether any exhaust component (i.e. unburned HC) could contribute to the NO_x conversion within the studied temperature range of 140 - 440 °C. The results showed negligible NO_x 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 NO_x 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 NO_x 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 NO_x (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 NO_x 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.

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 NO_x conversion followed closely the stoichiometric prediction at every inlet NO_2 concentration. This indicates the NO_x 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 NO_2/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 NO_2 , the SCR catalyst itself became more active in reducing NO_x due to further increase of NO_2 availability when H_2 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 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 NO_x conversion. The actual converted NO_x 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 NO_x 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 NO_x 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 NO_x 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 NO_x 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 NO_x conversion shown in Fig. 6a and Fig. 7c, confirming the increased NO_2 concentration was generally more beneficial to the low temperature NO_x removal. Due to the human and environmental hazard effects of NO_2 as well as the toxicity of NH_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_2 promotion. Further optimisation, which is out of the scope of this research work, could be performed 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 NO_2 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 NO_x reduction over an Ag/Al_2O_3 catalyst using actual diesel engine lean exhaust gas in real engine operation.

NO conversion to NO_2 was obtained over the Ag/Al_2O_3 with an oxidative promotion from H_2 . The formed NO_2 was suggested to be used in the SCR reaction immediately after its production and with the added NH_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_2 availability. The use of a Pt/Al_2O_3 based DOC in increasing the exhaust NO_2 level was also shown to improve significantly the SCR performance, which indicates the DOC simulated or even performed better the function of H_2 over the SCR catalyst. Hence one of the H_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 $200^\circ C$ or less in this case. However, this promotional effect of increased NO_2 concentration upstream the SCR catalyst was shown to be diminished by the increased reaction temperature, thus the SCR reaction’s H_2 dependence was reduced as well.

In general, the results suggest increasing the NO_2 concentration, either in the engine exhaust by means of combustion or from other catalytic aftertreatment and/or the Ag/Al_2O_3 itself, can improve significantly the H_2 – assisted NH_3 – SCR in low temperature NO_x control and at the same time reduce the system’s demand on H_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_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_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- NO_x activity while limiting any NH_3 and NO_2 slippage downstream the catalyst which could be released to the atmosphere.

Acknowledgements

The authors would like to thank Johnson Matthey for funding the project and providing the catalysts. The School of Mechanical Engineering at the University of Birmingham (UK) is gratefully acknowledged for the PhD School Scholarship to Mr. Wentao Wang. Engineering and Physical Science Research Council - EPSRC projects (EP/G038139/1), CREO projects (TSB/400176/149) and the Advantage West Midlands and the European Regional Development Fund as part of the Science City Research Alliance Energy Efficiency Project are also acknowledged for supporting the research work

References

- [1] A. Thiruvengadam, M.C. Besch, D.K. Carder, A. Oshinuga, M. Gautam, Influence of Real-World Engine Load Conditions on Nanoparticle Emissions from a DPF and SCR Equipped Heavy-Duty Diesel Engine, *Environ. Sci. Technol.*, 46 (2011) 1907-1913.
- [2] C. Misra, J.F. Collins, J.D. Herner, T. Sax, M. Krishnamurthy, W. Sobieralski, M. Burntitzki, D. Chernich, In-Use NO_x Emissions from Model Year 2010 and 2011 Heavy-Duty Diesel Engines Equipped with Aftertreatment Devices, *Environ. Sci. Technol.*, 47 (2013) 7892-7898.
- [3] M. Koebel, G. Madia, F. Raimondi, A. Wokaun, Enhanced Reoxidation of Vanadia by NO₂ in the Fast SCR Reaction, *J. Catal.*, 209 (2002) 159-165.
- [4] B. Shen, Y. Wang, F. Wang, T. Liu, The effect of Ce–Zr on NH₃-SCR activity over MnO_x(0.6)/Ce_{0.5}Zr_{0.5}O₂ at low temperature, *Chem. Eng. J.*, 236 (2014) 171-180.
- [5] U. De La Torre, B. Pereda-Ayo, J.R. González-Velasco, Cu-zeolite NH₃-SCR catalysts for NO_x removal in the combined NSR–SCR technology, *Chem. Eng. J.*, 207–208 (2012) 10-17.
- [6] R. Raj, M.P. Harold, V. Balakotaiah, Kinetic modeling of NO selective reduction with C₃H₆ over Cu-SSZ13 monolithic catalyst, *Chem. Eng. J.*, 254 (2014) 452-462.
- [7] A. Schuler, M. Votsmeier, P. Kiwic, J. Gieshoff, W. Hauptmann, A. Drochner, H. Vogel, NH₃-SCR on Fe zeolite catalysts – From model setup to NH₃ dosing, *Chem. Eng.*, 154 (2009) 333-340.
- [8] T. Du, H. Qu, Q. Liu, Q. Zhong, W. Ma, Synthesis, activity and hydrophobicity of Fe-ZSM-5@silicalite-1 for NH₃-SCR, *Chem. Eng. J.*, 262 (2015) 1199-1207.
- [9] B.M. Shakya, M.P. Harold, V. Balakotaiah, Simulations and optimization of combined Fe- and Cu-zeolite SCR monolith catalysts, *Chem. Eng. J.* In press
- [10] M. Richter, U. Bentrup, R. Eckelt, M. Schneider, M.M. Pohl, R. Fricke, The effect of hydrogen on the selective catalytic reduction of NO in excess oxygen over Ag/Al₂O₃, *Appl. Catal., B*, 51 (2004) 261-274.
- [11] M. Richter, R. Fricke, R. Eckelt, Unusual Activity Enhancement of NO Conversion over Ag/Al₂O₃ by Using a Mixed NH₃/H₂ Reductant Under Lean Conditions, *Catal. Lett.*, 94 (2004) 115-118.
- [12] S. Chansai, R. Burch, C. Hardacre, The use of Short Time on Stream (STOS) transient kinetics to investigate the role of hydrogen in enhancing NO_x reduction over silver catalysts, *J. Catal.*, 295 (2012) 223-231.
- [13] S. Tamm, S. Fogel, P. Gabrielsson, M. Skoglundh, L. Olsson, The effect of the gas composition on hydrogen-assisted NH₃-SCR over Ag/Al₂O₃, *Appl. Catal., B*, 136–137 (2013) 168-176.
- [14] S. Fogel, D.E. Doronkin, P. Gabrielsson, S. Dahl, Optimisation of Ag loading and alumina characteristics to give sulphur-tolerant Ag/Al₂O₃ catalyst for H₂-assisted NH₃-SCR of NO_x, *Appl. Catal., B*, 125 (2012) 457-464.
- [15] K.-i. Shimizu, J. Shibata, A. Satsuma, Kinetic and in situ infrared studies on SCR of NO with propane by silver–alumina catalyst: Role of H₂ on O₂ activation and retardation of nitrate poisoning, *J. Catal.*, 239 (2006) 402-409.
- [16] V.I. Pârvulescu, P. Grange, B. Delmon, Catalytic removal of NO, *Catal. Today*, 46 (1998) 233-316.
- [17] F. Klingstedt, K. Arve, K. Eräen, D.Y. Murzin, Toward Improved Catalytic Low-Temperature NO_x Removal in Diesel-Powered Vehicles, *A. Chem. Res.*, 39 (2006) 273-282.
- [18] D.E. Doronkin, S. Fogel, S. Tamm, L. Olsson, T.S. Khan, T. Bligaard, P. Gabrielsson, S. Dahl, Study of the “Fast SCR”-like mechanism of H₂-assisted SCR of NO_x with ammonia over Ag/Al₂O₃, *Appl. Catal., B*, 113–114 (2012) 228-236.
- [19] F.J.P. Schott, S. Steigert, S. Zuercher, M. Endisch, S. Kureti, Reactor design for the evaluation of diesel oxidation catalysts supported by sintered metal filters, *Chem. Eng. P*, 62 (2012) 54-58.
- [20] M.H. Wiebenga, C.H. Kim, S.J. Schmieg, S.H. Oh, D.B. Brown, D.H. Kim, J.-H. Lee, C.H.F. Peden, Deactivation mechanisms of Pt/Pd-based diesel oxidation catalysts, *Catal. Today*, 184 (2012) 197-204.
- [21] J.M. Herreros, S.S. Gill, I. Lefort, A. Tsolakis, P. Millington, E. Moss, Enhancing the low temperature oxidation performance over a Pt and a Pt–Pd diesel oxidation catalyst, *Appl. Catal. B*, 147 (2014) 835-841.
- [22] A. Abu-Jrai, A. Tsolakis, K. Theinnoi, A. Megaritis, S.E. Golunski, Diesel exhaust-gas reforming for H₂ addition to an aftertreatment unit, *Chem. Eng. J.*, 141 (2008) 290-297.
- [23] W. Wang, J.M. Herreros, A. Tsolakis, A.P.E. York, Ammonia as hydrogen carrier for transportation; investigation of the ammonia exhaust gas fuel reforming, *Int. J. Hydrogen Energ.*, 38 (2013) 9907-9917.
- [24] J. Giménez-Mañogil, A. Bueno-López, A. García-García, Preparation, characterisation and testing of CuO/Ce_{0.8}Zr_{0.2}O₂ catalysts for NO oxidation to NO₂ and mild temperature diesel soot combustion, *Appl. Catal. B*, 152–153 (2014) 99-107.
- [25] N. Guillén-Hurtado, I. Atribak, A. Bueno-López, A. García-García, Influence of the cerium precursor on the physico-chemical features and NO to NO₂ oxidation activity of ceria and ceria–zirconia catalysts, *J. Mol. Catal., A*, 323 (2010) 52-58.
- [26] P.S. Metkar, V. Balakotaiah, M.P. Harold, Experimental and kinetic modeling study of NO oxidation: Comparison of Fe and Cu-zeolite catalysts, *Catal. Today*, 184 (2012) 115-128.

- [27] M. Hori, Y. Koshiishi, N. Matsunaga, P. Glaude, N. Marinov, Temperature dependence of NO to NO₂ conversion by n-butane and n-pentane oxidation, *P. Comb. Ins.*, 29 (2002) 2219-2226.
- [28] S.R. Katare, J.E. Patterson, P.M. Laing, Diesel aftertreatment modeling: A systems approach to NO_x control, *Industrial and Engineering Chem. Res.*, 46 (2007) 2445-2454.
- [29] K. Hauff, U. Tuttlies, G. Eigenberger, U. Nieken, Platinum oxide formation and reduction during NO oxidation on a diesel oxidation catalyst - Experimental results, *Appl. Catal., B: Environmental*, 123-124 (2012) 107-116.
- [30] A. Boubnov, S. Dahl, E. Johnson, A.P. Molina, S.B. Simonsen, F.M. Cano, S. Helveg, L.J. Lemus-Yegres, J.D. Grunwaldt, Structure-activity relationships of Pt/Al₂O₃ catalysts for CO and NO oxidation at diesel exhaust conditions, *Appl. Catal., B*, 126 (2012) 315-325.
- [31] I. Lefort, J.M. Herreros, A. Tsolakis, Reduction of Low Temperature Engine Pollutants by Understanding the Exhaust Species Interactions in a Diesel Oxidation Catalyst, *Environ. Sci. & Technol.* 48 (2014) 2361-2367.
- [32] M.M. Azis, H. Harelind, D. Creaser, Kinetic modeling of H₂ - assisted C₃H₆ selective catalytic reduction of NO over silver alumina catalyst, *Chem. Eng. J.*
- [33] M.M. Azis, H. Härelind, D. Creaser, Microkinetic modeling of H₂-assisted NO oxidation over Ag–Al₂O₃, *Chem. Eng. J.*, 221 (2013) 382-397.
- [34] J.M. Herreros, P. George, M. Umar, A. Tsolakis, Enhancing selective catalytic reduction of NO_x with alternative reactants/promoters, *Chem. Eng. J.*, 252 (2014) 47-54.
- [35] C. Ciardelli, I. Nova, E. Tronconi, D. Chatterjee, B. Bandl-Konrad, M. Weibel, B. Krutzsch, Reactivity of NO/NO₂–NH₃ SCR system for diesel exhaust aftertreatment: Identification of the reaction network as a function of temperature and NO₂ feed content, *Appl. Catal., B: Environmental*, 70 (2007) 80-90.
- [36] K. Theinnoi, S. Sitshebo, V. Houel, R.R. Rajaram, A. Tsolakis, Hydrogen Promotion of Low-Temperature Passive Hydrocarbon-Selective Catalytic Reduction (SCR) over a Silver Catalyst, *Energ. Fuel.*, 22 (2008) 4109-4114.
- [37] S. Moon Lee, S. Su Kim, S. Chang Hong, Systematic mechanism study of the high temperature SCR of NO_x by NH₃ over a W/TiO₂ catalyst, *Chem. Eng. Sci.*, 79 (2012) 177-185.
- [38] J. Wang, Z. Peng, Y. Chen, W. Bao, L. Chang, G. Feng, In-Situ Hydrothermal Synthesis of Cu-SSZ-13/Cordierite for the Catalytic Removal of NO_x from Diesel Vehicles by NH₃, *Chem. Eng. J.*
- [39] B. Opitz, M. Bendrich, A. Drochner, H. Vogel, R.E. Hayes, J.F. Forbes, M. Votsmeier, Simulation study of SCR catalysts with individually adjusted ammonia dosing strategies, *Chem. Eng. J.*, 264 (2015) 936-944.

List of figures

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 NH₃ additions with a fixed H₂ addition (a) NO₂ and (b) NH₃.

Figure 5: Effect of hydrogen addition at 3 Bar IMEP, (a) NO_x reduction with and without the increased NO₂ concentration (b) NO₂ consumed over the SCR and (c) experimentally and calculated (based on Fast – SCR stoichiometry) NO_x conversion.

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

Figure 7: NO_x 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.

List of tables

Table 1: Engine conditions and average emissions.

Table 2: Summarise of conditions in each experimental run.

ACCEPTED MANUSCRIPT

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) NO_x reduction with and without the increased NO₂ concentration (b) NO₂ consumed over the SCR and (c) experimentally and calculated (based on Fast – SCR stoichiometry) NO_x conversion.

Figure 6: Effect of hydrogen on NO_x conversion at 2 Bar IMEP at SCR catalyst inlet temperature of 180 °C (a) 2000, 4000 and 8000 ppm H₂ addition upstream SCR and (b) experimental and calculated (based on Fast – SCR stoichiometry) NO_x conversion at 2000 and 4000 ppm H₂ 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: NH₃ slippage after the SCR catalyst at 2 Bar IMEP.

Table 1: Engine conditions and average emissions.

Engine Load (Nm)	IMEP* (bar)	NO (ppm)	NO ₂ (ppm)	THC** (ppm)	CO (ppm)	CO ₂ (%)	O ₂ (%)	H ₂ O (%)
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	0, 1000, 2000, 3000, 4000, 6000	NA	NA
		3	230 (exhaust)				
		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 NO _x)
				230 (furnace)			
		3	230 (exhaust)	150 (furnace)	0	2000, 4000, 8000	530 (match exhaust NO _x)
				200 (furnace)			
				230* (furnace)			
		4	300 (exhaust)	150 (furnace)	0	8000	730 (match exhaust NO _x)
				200 (furnace)			
				250 (furnace)			
				300* (furnace)			
Transient		4	300 (exhaust)	150 – 500 (ramp)	0	8000	0

* SCR inlet temperature matched the exhaust temperature

Appendix

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

NO_x REDUCTION FROM LOW TEMPERATURE DIESEL EXHAUST

Highlights

- NO_2 formation in $\text{Ag}/\text{Al}_2\text{O}_3$ catalyst was found to increase with H_2 addition
- Increased NO_2 formation on $\text{Ag}/\text{Al}_2\text{O}_3$ enhanced its NH_3 – SCR activity at low reaction temperature
- NO_2 formation prior to $\text{Ag}/\text{Al}_2\text{O}_3$ (i.e. engine or DOC) will benefits the NH_3 – SCR activity
- The NO_2 promotion diminished at high temperature