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Improving the low temperature NO_x reduction activity over a $Ag-Al_2O_3$ catalyst

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ABSTRACT

Silver-alumina ($Ag-Al_2O_3$) catalysts are susceptible to deactivation by nitrates and/or carbon species deposition, especially at low temperatures. A prototype catalyst (PC) was used to cleanse the diesel exhaust by reducing potential catalyst poisoning species and possibly generate more reactive species which would aid the SCR catalyst NO_x reduction activity. The PC was located upstream the SCR catalyst and its influence on the passive SCR catalyst NO_x activity was dependant on the engine exhaust gas temperature, hydrogen concentration (50–5000 ppm) and space velocity (SV).

Nevertheless, the PC was found to have significant influence on the reduction of HCs, CO and particulate matter (PM) across all engine operating conditions. During HC-SCR at low temperatures, there was sufficient HC species available for the reduction of NO_x (peaking at ~80%) over the $Ag-Al_2O_3$ catalyst. However, there was a decrease in NO_x conversion at higher engine exhaust gas temperatures, attributed to the reduced HC concentrations relative to the NO_x produced by the engine and also the HC oxidation reaction being more predominant over the HC-NO_x reduction reaction. At these particular conditions the active injection of HC species (engine fuel) was necessary for improved NO_x reduction activity over the Ag-based SCR catalyst. HC speciation in the exhaust gas shows that the PC reduces small chain HCs but has small influence in reduction of toluene and >C7 hydrocarbons.

Of the three investigated space velocities, the best NO_x conversion was observed for the medium value of ~20,000 h^{-1}. The lower (15,000 h^{-1}) and higher (25,000 h^{-1}) space velocities yielded results that were similar to those without the use of the PC. Hence, a careful balance between exhaust gas temperature, SV and reactants is therefore necessary for the best NO_x reduction activity.

1. Introduction

With ever more stringent emission regulations being enforced by the environmental governing bodies with regards the emissions from automobiles; diesel after-treatment is now a necessary component in the emissions reduction strategy. Among the most desirable after-treatment technologies for NO_x emissions reduction is hydrocarbon selective catalytic reduction (HC-SCR) over $Ag-Al_2O_3$ catalysts, which utilises hydrocarbons (HCs) as the reducing agent for NO_x. Some advantages of this technology include its cost effectiveness and simplicity to implement.

However, NO_x reduction activity is currently interdependent on other technologies, such as diesel particulate filters (DPFs) and diesel oxidation catalysts (DOCs). The DPF and DOC technology's primary role is to reduce emissions of CO, HCs and PM, which are harmful components present in diesel engine exhaust gas. At the same time, the reduction of these has another important benefit, since cleaner exhaust gas at the inlet of a selective catalytic reduction (SCR) catalyst (located downstream of the DOC/DPF in a typical configuration) improves its durability and efficiency at reducing NO_x. A DPF is designed to trap and periodically or continuously burn off the accumulated particulate matter (PM) [1–4]. The soot accumulated in the DPF has to be kept below a balanced threshold so as not to cause undesirable back pressures in the exhaust tailpipe [3] which could reduce the fuel economy and engine durability. On the other hand, a common DOC is designed to continuously oxidise carbon monoxide, gas phase hydrocarbons, and the soluble organic fraction (SOF) of PM to carbon dioxide (CO_2) and water (H_2O). Since the diesel engine operates on a lean burn cycle, there is sufficient oxygen (O_2) necessary for the DOC oxidation reactions.

In HC-SCR, silver-alumina ($Ag-Al_2O_3$) catalysts are being widely researched due to their proven ability to reduce NO_x by utilising various HC species in the presence of hydrogen (H_2), at relatively

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Abbreviations: CPC, condensation particle counter; cpsi, cells per square inch; DMA, differential mobility analyser; DOC, diesel oxidation catalyst; DPF, diesel particulate filter; FID, flame ionization detector; GC, gas chromatography; HC, hydrocarbons; HC-SCR, hydrocarbon-selective catalytic reduction; NDIR, non-dispersive infraRed; NO_x, nitrogen oxides; PC, prototype catalyst; PM, particulate matter; SMPS, scanning mobility particle sizer; SOF, soluble organic fraction; SV, space velocity; ULSD, ultra-low sulphur diesel.

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low temperatures [5–10]. Nonetheless, they are rather sensitive to the amount and speciation of the HCs present in the exhaust. Excessive amounts of HCs in the exhaust, at low temperature, even in the presence of H_2, can have an adverse effect on the NO_x reduction activity of the catalyst primarily due to carbon-containing species adsorption onto the Ag-Al_2O_3 catalyst surface [9,11,12]. Surface nitrates formation has also been cited as a major contributor to SCR catalyst fouling [13]; a process that can be reversed by the addition of H_2 into the exhaust gas.

Diesel engine operating conditions play an important role in regulating the exhaust gas temperature of the engine. High load, high speed engine operation results in increased exhaust gas temperatures. With increasing exhaust gas temperature the HC oxidation reaction is more prominent, resulting in decreased reactive HC species availability for the SCR of NO_x over the Ag-Al_2O_3 catalysts. As a result, the H_2 and HC amounts present in the exhaust need to be optimized for specific engine operating conditions.

In the present investigation, the promotional effect of H_2 was studied for full-scale diesel engine exhaust utilising a prototype diesel oxidation catalyst (PC). The results presented show how the activity and/or durability of Ag-Al_2O_3 catalysts can be possibly improved for NO_x reduction in real diesel engine exhaust gas.

2. Experimental

2.1. Engine

The engine used in these experiments was direct injection, single cylinder experimental diesel engine. More detailed specifications have been given in previous publications [14,15]. The engine tailpipe and catalyst arrangement is shown in Fig. 1 below.

2.2. Catalysts

The catalysts comprised of a prototype oxidation catalyst (PC) and two Ag-Al_2O_3 catalysts (for greater active volume) supported on identical ceramic monolith bricks (Ø 4.66 × L3 in.). The PC was placed upstream of the SCR catalysts, in a reactor connected to the exhaust tailpipe as shown in Fig. 1.

- *Prototype monolith catalyst* (PC): The catalyst comprised of a prototype formulation developed by Johnson Matthey Plc, whose purpose was to (i) adsorb hydrocarbons and oxidise CO at low exhaust temperatures and (ii) to release hydrocarbons and/or oxidise C-containing species (i.e. CO, PM and some HC species) at high exhaust gas temperatures.
- *HC-SCR Ag-Al_2O_3 monolith catalysts*: A silver catalyst (2 wt.%) was prepared by impregnating γ-alumina (surface area ~ 150 m^2/g) with aqueous $AgNO_3$, before drying and calcining (in air for 2 h at 500 °C).

The catalysts were made into separate aqueous suspensions, which were then uniformly coated onto ceramic monolith substrates with a high cell density (600 cpsi).

2.3. Fuel

Ultra-low sulphur diesel (ULSD) was the sole fuel used in this investigation. The fuel specifications are as listed in Table 1, below.

Table 1
The ULSD fuel specifications.

Parameter	Value
Cetane number	54.1
Density @ 15 °C (kg/m^3)	833.3
50% distillation (°C)	278
95% distillation (°C)	340.4
Viscosity @ 40 °C (cSt)	2.83
Sulphur (mg/kg)	7
Carbon (wt.%)	85.3
Hydrogen (wt.%)	13.9

2.4. Test conditions

The effect of the PC on the Ag-Al_2O_3 catalyst activity with hydrogen addition (0, 700, 1500, 3000 and 5000 ppm) from a certified bottled source (including ~50–100 ppm from the combustion process itself), were examined for twelve steady-state engine operating conditions (speed–load). In order to investigate the effect of the space velocity over the Ag-Al_2O_3 catalyst, the engine speeds tested were 1800, 1500 and 1200 rpm, resulting in space velocities of 25,000, 20,000 and 15,000 h^{-1}, respectively.

At each engine speed, the effect of exhaust gas temperature and composition were investigated through various engine loads (12, 25, 50 and 75%). Engine load was defined as the percentage of the maximum torque achievable at each engine speed, running the engine with the same fuel. The NO_x, HC, HC:NO_x ratio and exhaust gas temperature were recorded at the inlet of the Ag-Al_2O_3 catalysts and are shown in Tables 2 and 3.

2.5. Experimental procedure and equipment

2.5.1. Exhaust gas analysis

A Horiba Mexa 7100DEGR analyser was used to measure the concentrations of NO_x ($NO + NO_2$) by chemiluminescence; CO and CO_2 by non-dispersive infrared (NDIR); O_2 by an electrochemical method and hydrocarbons (HCs) by flame ionization detection (FID). The H_2 concentration in the exhaust gas at the SCR catalyst inlet was measured using a gas chromatography (GC) analyser.

2.5.2. Particulate matter analysis

The particulate sampling system used a scanning mobility particle sizer (SMPS) spectrometer manufactured by TSI. It comprised of an electrostatic classifier series 3080, a 3081 differential mobility analyser (DMA) and a model 3775 condensation particle counter (CPC). The exhaust gas dilution ratio was preset to 100:1 (using a properly calibrated dilutor) and particle distributions were measured in the 10–500 nm range. Exhaust samples were taken from the same position in the exhaust manifold for both the SMPS and the exhaust gas analyser.

2.5.3. Hydrocarbon species analysis

Quantitative hydrocarbon analysis (C_1–C_7) at the inlet of the SCR was performed on a Hewlett Packard Model 5890 Gas Chromatograph-FID equipped with a 25 m × 0.32 mm i.d. capillary column with a 10 μm film thickness PoraPLOT Q. The gas samples were introduced into a gas-sampling valve outfitted with a 2.5 ml sample loop. To calibrate the GC-FID for hydrocarbon species (i.e. qualitative and quantitative) analysis, several standard mixtures of paraffins and olefins from C_1 to C_7 with known concentrations were used.

3. Results and discussion

3.1. PC effect on engine exhaust emissions

The prototype catalyst's primarily design role was to reduce C species such as HCs, CO and part of the PM from diesel engine exhaust gas which typically has relatively low NO_x reduction efficiencies at low temperatures over Ag SCR catalysts. Its effectiveness at reducing these particular emissions is illustrated in

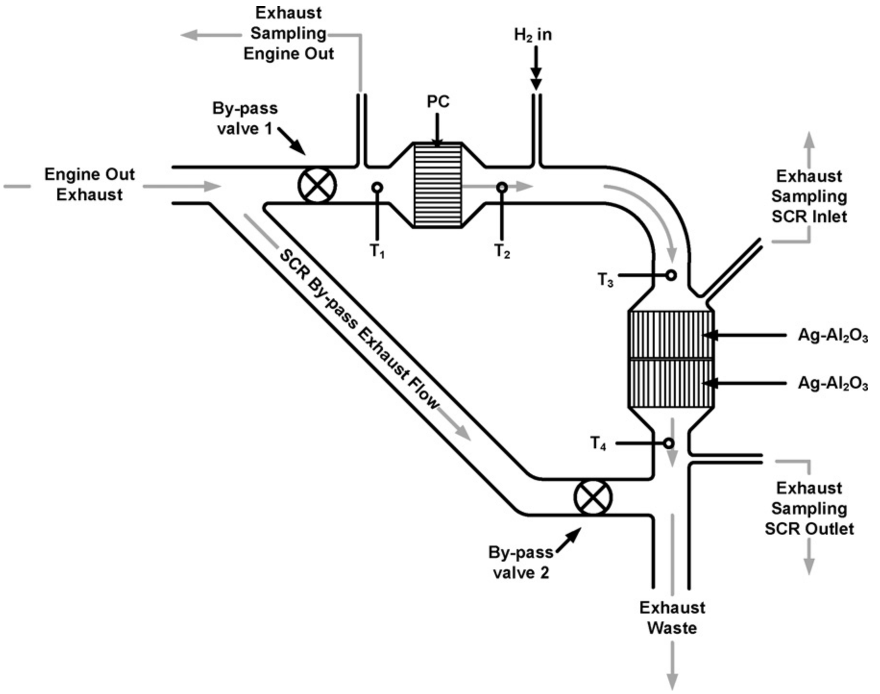

Fig. 1. Single cylinder Lister Petter engine exhaust tailpipe, showing the catalyst arrangement, exhaust sampling points and temperature measurement points.

Figs. 2 and 3. The catalyst HC reduction efficiency is dependent on the engine exhaust gas temperature. As indicated from the HC conversion under the same SV (i.e. engine speed) the prototype catalyst achieved its light-off (50% conversion) temperature only at high engine loads (i.e. 50 and 75%).

The CO reduction efficiency was very high (> 98%) across all tested conditions (Tables 2 and 3) due to CO requiring less energy to oxidise compared to HC molecules. On the other hand, the NO_x reduction activity of the PC was relatively low as Fig. 3 illustrates, with reductions of only ~20% being achieved at the higher temperatures in the engine load operating range of 50 and 75% (>250 °C). This means that the decline in the concentration of HCs is partially due to the NO_x-reducing reactions taking place over the prototype catalyst. In the lower temperature region (<240 °C), corresponding to 12 and 25% engine loading, there was less than ~10% NO_x reduction.

For all the tested engine load conditions, the space velocity over the PC seemed not to affect its performance significantly for the reductions of CO, HC and NO_x emissions. Overall, it could be concluded that the PC only needs to reach light-off temperature to maintain its effectiveness across a wide range of operating conditions.

3.2. *PC effect on particle size distribution (1200 and 1800 rpm 50% load)*

The particle size distribution of the different engine speed–load conditions yielded different results, but from our experimental findings the characteristics observed followed a similar trend, therefore to avoid repetition, only the analysis of the highest and lowest engine speeds of 1800 and 1200 rpm at 50% load respectively will be assessed. From the particle number analysis (Fig. 4),

Table 2
SCR inlet parameters without the implementation of the prototype catalyst.

1800 rpm SV = 25,000 h^{-1}	Engine load (%)	12	25	50	75
	NO_x (ppm)	388	494	806	1089
	CO (ppm)	174	126	111	257
	HC (ppm)	367	390	422	465
	HC:NO_x ratio	0.95	0.79	0.52	0.43
	O_2 (%)	16.5	15.87	13.85	11.74
	T_3 (°C)	165	224	285	327
1500 rpm SV = 20,000 h^{-1}	Engine load (%)	12	25	50	75
	NO_x (ppm)	373	523	815	1064
	CO (ppm)	187	164	133	153
	HC (ppm)	343	349	396	425
	HC:NO_x ratio	0.92	0.67	0.49	0.40
	O_2 (%)	17.02	16.15	14.1	11.77
	T_3 (°C)	159	197	240	306
1200 rpm SV = 15,000 h^{-1}	Engine load (%)	12	25	50	75
	NO_x (ppm)	361	457	668	993
	CO (ppm)	288	230	251	1261
	HC (ppm)	333	364	380	480
	HC:NO_x ratio	0.92	0.80	0.57	0.48
	O_2 (%)	17.03	15.98	13.57	10.68
	T_3 (°C)	137	177	237	297

Table 3
SCR inlet parameters with the implementation of the prototype catalyst.

1800 rpm SV = 25,000 h^{-1}	Engine load (%)	12	25	50	75
	NO$_x$ (ppm)	341	406	687	1035
	CO (ppm)	0	0	0	5
	HC (ppm)	228	234	267	292
	HC:NO$_x$ ratio	0.67	0.58	0.39	0.28
	O$_2$ (%)	16.91	15.74	13.52	11.1
	T_3 (°C)	190	231	299	342
1500 rpm SV = 20,000 h^{-1}	Engine load (%)	12	25	50	75
	NO$_x$ (ppm)	356	480	660	837
	CO (ppm)	1	1	1	4
	HC (ppm)	289	276	217	189
	HC:NO$_x$ ratio	0.81	0.58	0.33	0.23
	O$_2$ (%)	16.79	15.75	13.70	11.32
	T_3 (°C)	171	207	273	335
1200 rpm SV = 15,000 h^{-1}	Engine load (%)	12	25	50	75
	NO$_x$ (ppm)	341	443	544	840
	CO (ppm)	2	0	1	5
	HC (ppm)	211	227	157	222
	HC:NO$_x$ ratio	0.62	0.51	0.29	0.27
	O$_2$ (%)	17.00	15.88	13.10	9.94
	T_3 (°C)	152	183	260	340

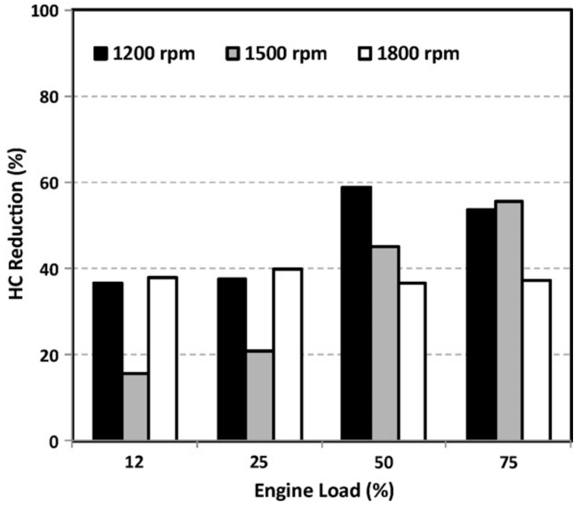

Fig. 2. Reduction in hydrocarbon (HC) emissions over the PC for the specified engine loads.

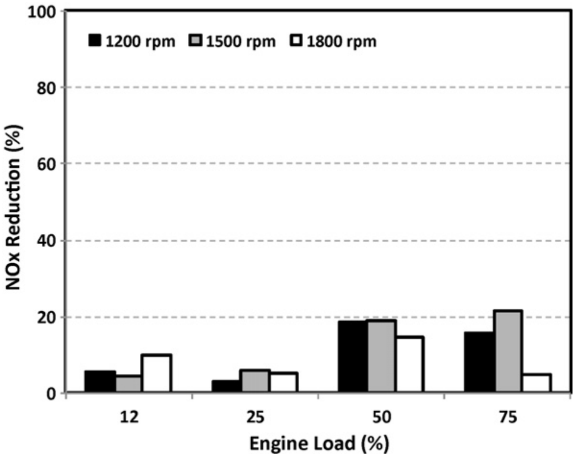

Fig. 3. The PC effect on the overall NO$_x$ to N$_2$ conversion for the respective engine speeds and loads studied.

it was generally found that the particle number concentration, in almost all the diameter range measured, was reduced.

Through a mass analysis, the PC can be seen to effectively reduce the total particle mass and number from the diesel exhaust gas, particularly as the engine loading was increased (Figs. 5 and 6). It can also be seen that the reduction in particle number along the PC is, in general, higher than the reduction in mass. This indicates that the PC is more effective in removing the smaller particles, which are formed (totally or in a high proportion) by hydrocarbons. It is well known that hydrocarbons are more easily oxidise than soot in an oxidation catalyst.

By reducing both the total particulate mass and number in the diesel exhaust, the NO$_x$ reduction mechanism over Ag-Al$_2$O$_3$ cata-

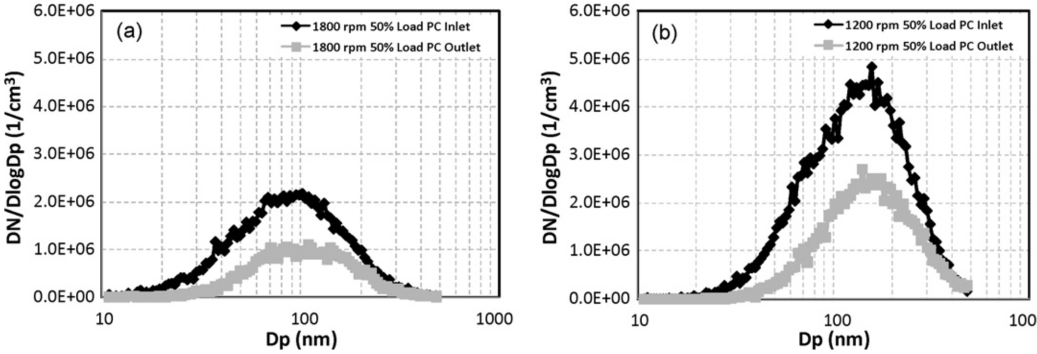

Fig. 4. The total particle number distribution of the diesel engine exhaust with and without the prototype catalyst for: (a) 1800 rpm and 50% load and (b) 1200 rpm and 50% load.

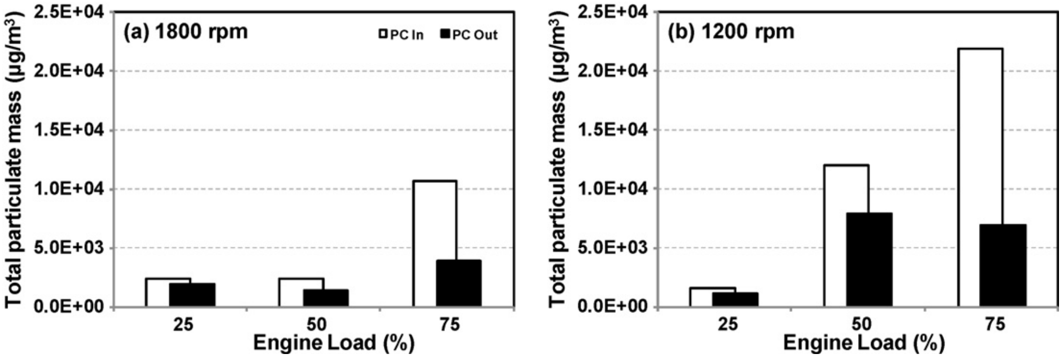

Fig. 5. Total particulate mass concentration in the exhaust gas without (PC In) and with (PC Out) the prototype catalyst.

lysts could be improved leading to better efficiencies, due to lower impurities. As a result, a study of the NO_x activity over Ag-Al_2O_3 catalysts was necessary in order to conclusively show that the activity of the catalysts could be improved through the use of the PC by limiting the amount of possible poisoning species (in the diesel exhaust gas) leading to reduced deactivation mechanisms.

3.3. PC effect on C_1–C_7 hydrocarbons (1200 and 1800 rpm, 25 and 75% load)

Analysis of the HC species from the combustion process itself was carried out for short chain species (C_1–C_7). The HCs shown in Tables 2 and 3 are representative of the total C_1 count and since the experimental study was focusing on 'passive; HC-SCR over Ag-Al_2O_3 catalysts, speciation was a necessary component for trend analysis during NO_x catalysis. For trend analysis, the engine conditions chosen for this part of the study were the highest speed of 1800 rpm and the lowest speed of 1200 rpm both at engine loads of 25 and 75%.

Varying engine speed at low engine load (25%) showed only a slight effect on the C_1–C_7 HC species distribution pattern and magnitude (Fig. 7). It was predominantly of the order toluene > ethylene > methane > propylene in both conditions. At 1200 rpm in particular (Fig. 7a), the poor toluene reduction of 15% reflects the difficulty of oxidization of this aromatic HC compound. This can be attributed to the combined effects of exhaust gas temperature and the reduced space velocity, which lowers the effective heat transfer towards an exothermic reaction.

At the higher engine load (75%), greater variation is observed in the inlet HC species especially at 1200 rpm. At this condition, low toluene output from the engine was measured but with an increase in the other light species. Included in the other light HC constituents was the photo-chemically reactive compound of 1,3-butadiene, which is a known carcinogen according to the United States Environmental Protection Agency (US-EPA). In contrast, at 1800 rpm a significantly higher toluene concentration was observed before the PC, alongside with reduced amount of light alkanes and alkenes, suggesting a less complete combustion for each engine cycle. This combustion completeness discrepancy between the HC species emissions from the engine could be attributed to the difference in residual time inside the combustion chamber due to the difference in engine speed. The rest of undetected HC species making the total C_1 count (Tables 2 and 3) are therefore the heavier HCs (i.e. greater than C_7).

From analysis of the engine out and PC out emissions (Figs. 7 and 8), it can be observed that the PC was very effective at removing the small amounts of light HCs which are known to be un-reactive at low exhaust gas temperature in Ag-Al_2O_3 NO_x catalysis [12]. Comparatively, of the HC species characterised, toluene (an aromatic HC) seems to be the major output product from the combustion process of ULSD, before and after the PC. Other small chain HCs can be present but only in small quantities. Arve et al. [16] in their study on a cascade concept involving Ag/alumina and a Cu-ZSM-5, found that toluene was not very good as a reductant over the Ag catalyst. They found that the addition of toluene into the exhaust gas stream into the Ag catalyst resulted in an increase in the temperature for initial NO catalytic activity. These findings are in agreement with Breen et al. [17] who in their study on the sulphur tolerance of Ag/γ-Al_2O_3 catalysts, found that the addition of toluene to the exhaust stream had a negating effect on the temperature at which the Ag catalyst showed significant NO_x activity. It can therefore be surmised that the presence of aromatics in the exhaust gas during the HC-SCR of NO_x is a major disadvantage for Ag-Al_2O_3 catalysts.

3.4. H_2-effect on HC-SCR of NO_x with PC use

The PC was used in conjunction with H_2 addition (700–5000 ppm) in order to study its effectiveness on SCR

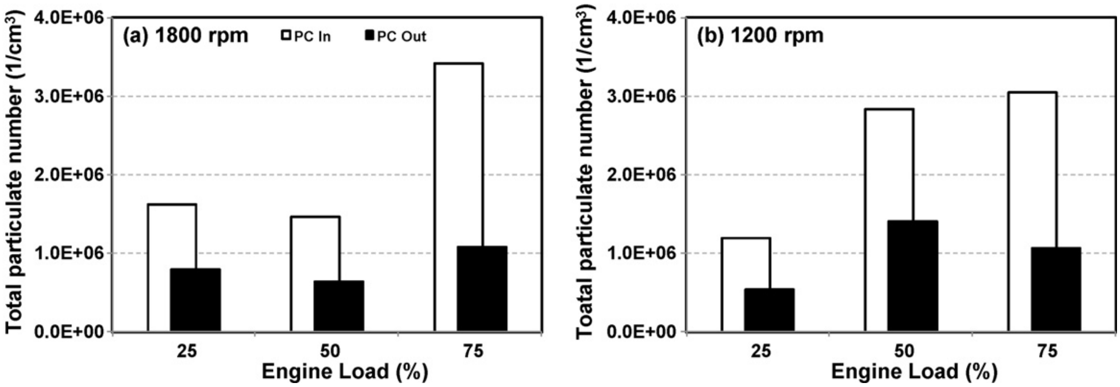

Fig. 6. Total particulate number concentration in the exhaust gas without (PC In) and with (PC Out) the prototype catalyst.

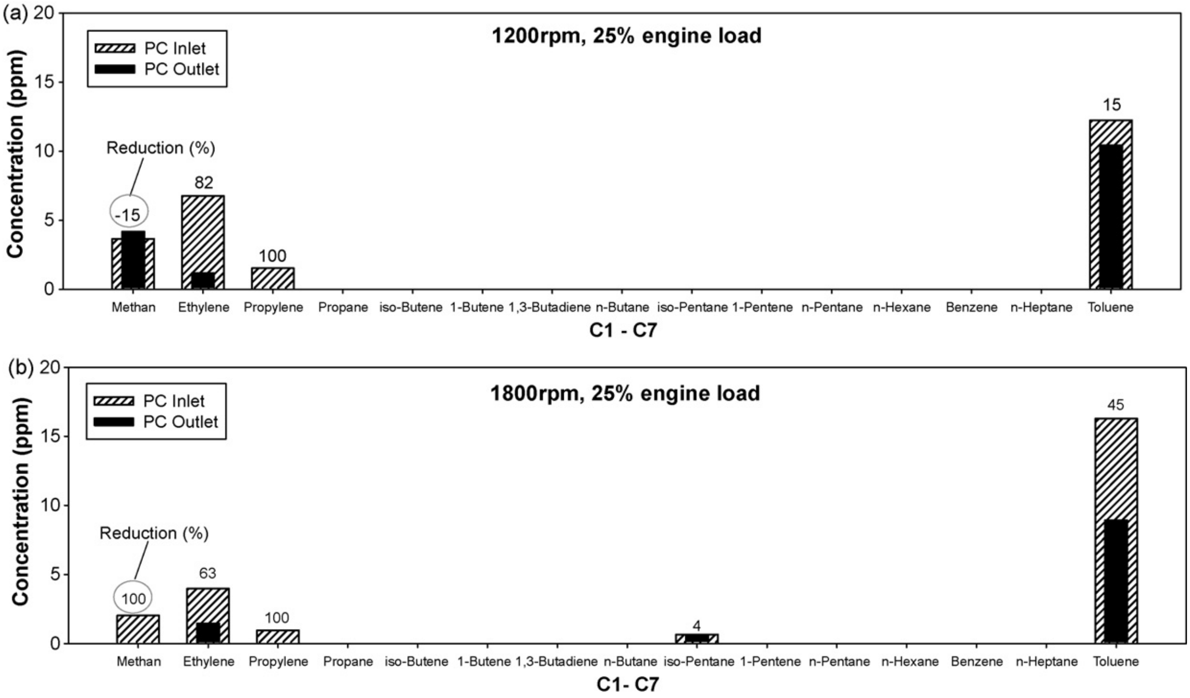

Fig. 7. Comparison of the variation in short chain (C_1–C_7) HC species at the engine speed of 1200 and 1800 rpm operating at an engine load of 25%.

of NO_x over Ag-Al_2O_3 with reduced impurities. This was to check whether there was any notable improvement in the NO_x reduction activity of the Ag-Al_2O_3 catalysts as compared to a similar study [18] involving no PC use, where there was suspicion of SCR catalyst deactivation due to excess HC adsorption at low temperatures. A simplified mechanism of the HC-SCR reaction involves the activation of NO to NO_2 and then the reaction of this NO_2 with HC to form nitrogen (N_2), carbon dioxide (CO_2) and water (H_2O), according to Eqs. (1) and (2) below:

$$2NO + O_2 \rightarrow 2NO_2 \qquad (1)$$

$$CH_2 + \tfrac{3}{2}NO_2 \rightarrow \tfrac{3}{4}N_2 + CO_2 + H_2O \qquad (2)$$

It can be surmised (on a molar basis) that the HC amount (ppm) can reduce the equivalent of 1.5 times the NO_x (ppm),

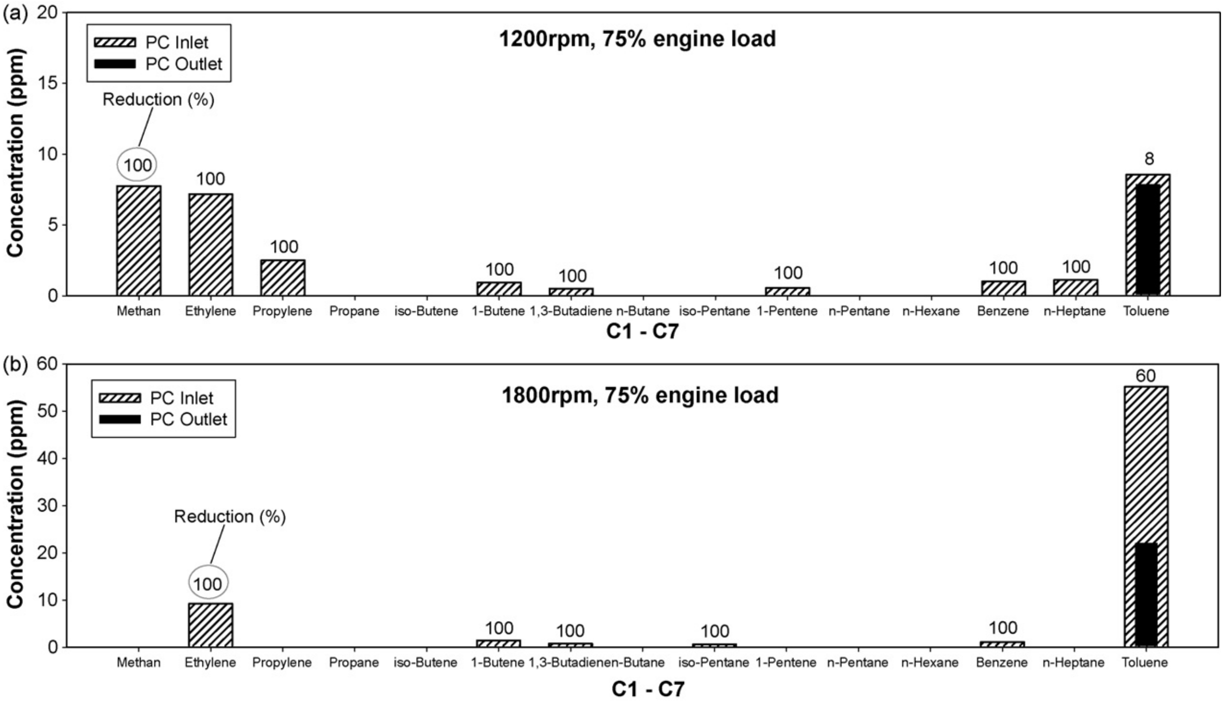

Fig. 8. A comparison of the variation in short chain (C_1–C_7) HC species at the engine speed of 1200 and 1800 rpm operating at an engine load of 75%.

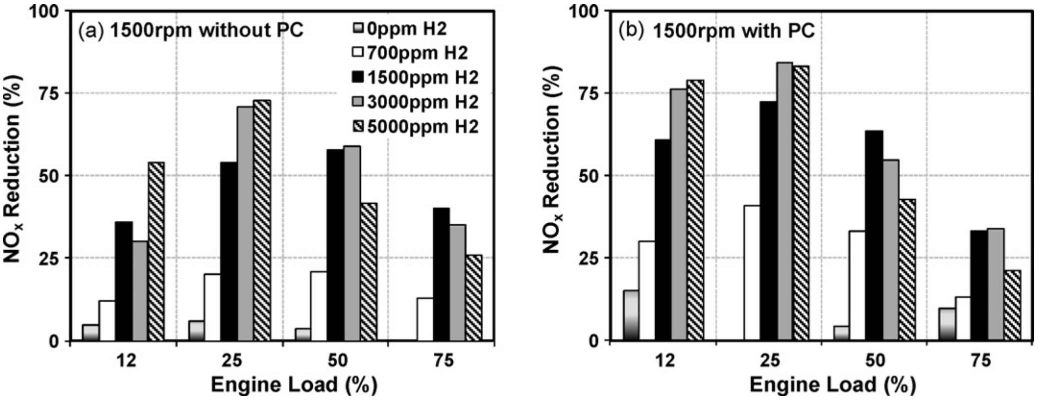

Fig. 9. Effect of varied H_2 addition on Ag-Al_2O_3 NO_x reduction activity: (a) without PC use and (b) with PC use, at 1500 rpm.

since the NO and NO_2 in reaction are 1:1 equivalent (Eq. (1)). It is generally accepted that there are intermediate reactions that occur between Eqs. (1) and (2) which form the critical path of reaction for the reduction of NO_x. This simplified NO_x reduction mechanism version is to show that the reaction of HC and NO_x does not have to be at 1:1 (Eq. (2)) or higher to achieve complete NO_x reductions in diesel exhaust gas.

To illustrate the effect of hydrogen addition on the SCR catalysts, the results for the engine speed of 1500 rpm have been chosen since common similarities were observed for the other engine speeds (i.e. 1200 and 1800 rpm). Without the addition of H_2 to the exhaust, there was no significant NO_x reduction observed across the whole engine speed–load range for both cases (Fig. 9). However, an increase in hydrogen addition to the diesel exhaust gas upstream the silver SCR catalysts had a corresponding positive effect on NO_x reduction, but predominantly in the low temperature (low load) regions, where higher HC:NO_x ratios were observed. With higher engine temperature, the HC:NO_x ratios and NO_x conversion activity were reduced; with peak NO_x conversions being observed for lower H_2 additions at these particular conditions. This highlights the necessity to optimize the H_2 content depending on the exhaust temperature and the HC:NO_x ratio, based on the reactive fraction of HC species. The low HC:NO_x ratios were due to the higher engine out NO_x emissions as the engine load was increased. Furthermore, the presence of toluene does not aid the HC-SCR reaction over Ag-Al_2O_3 catalysts [16]. The reduced maximum NO_x conversion and HC:NO_x ratios (at higher loads) is in agreement with several authors [19,20,12,21], who have reported that the HC:NO_x ratio has significant influence in the amount of NO_x reduced over the Ag-Al_2O_3 SCR catalyst; with increased NO_x conversion being observed at the higher HC:NO_x ratios.

An important reported key step in low temperature NO_x reduction activity lies in hydrogen's reductive activation of molecular oxygen species involved in the oxidative activation of HCs [8,21,22]. The improvement in overall NO_x conversion with the use of the PC for the 1500 rpm engine speed (Fig. 9b), was possibly due to higher chain HC activation over the PC surface, coupled with the H_2 activation of HCs after the PC, making them more reactive. However,

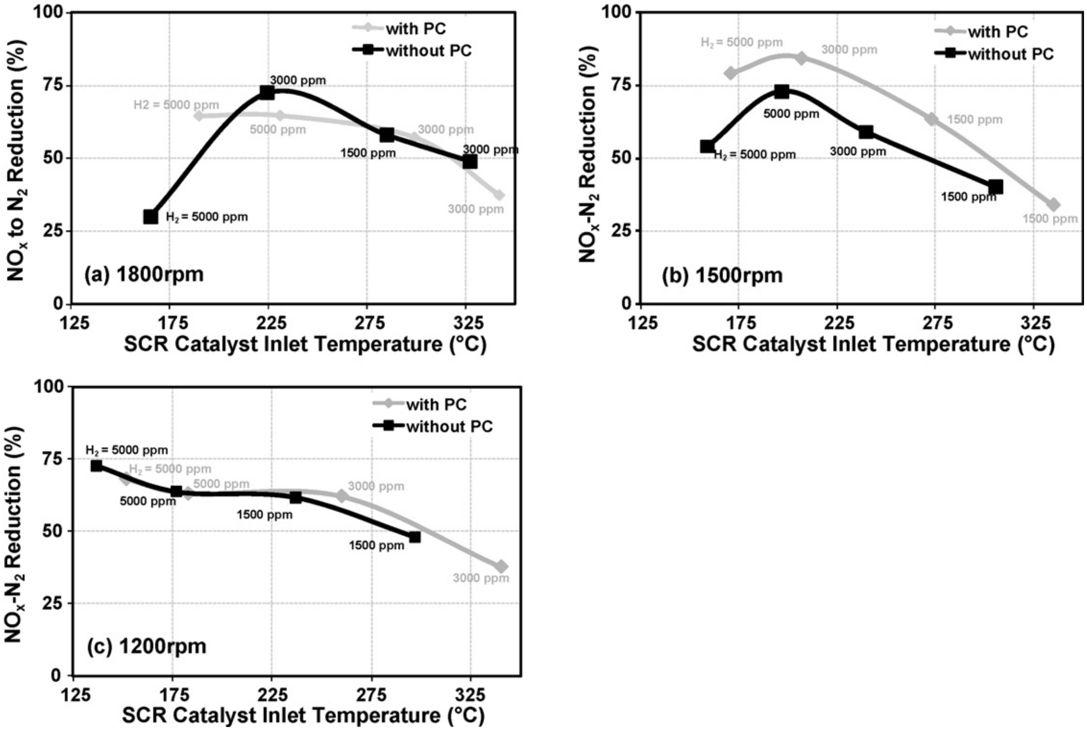

Fig. 10. The maximum NO_x conversion with H_2 addition and PC use for (a) 1800 rpm, (b) 1500 rpm and (c) 1200 rpm, for varying SCR inlet exhaust temperature (i.e. 12, 25, 50 and 75% load, respectively).

according to the results herein, the most probable explanation lies in the reduction of poisoning species, e.g. unreactive HCs, soot particles etc, as illustrated and discussed in the above sections. Thus, despite the fact that the HC:NO_x ratio was reduced by using the PC, we have proved that the same or even better NO_x reduction can be achieved over the SCR catalyst if it is fed with either less poisoning species or more active HCs, especially at the low temperature regions (12 and 25% load). However, the space velocity (SV) seemed to play an important role in the PC's effectiveness at improving NO_x reduction at all conditions as discussed in the following section.

When using the PC, the best NO_x conversion peaked at ~82% at low engine load conditions and at an engine speed of 1500 rpm. Exhaust gas temperature, HC:NO_x ratio and SV are all among the influential factors in NO_x reduction activity and given the peak conversion occurring at the 25% engine load; near optimum values of the influential parameters may have been attained. While at the higher engine load (higher temperatures), there was not enough active HCs after the PC for NO_x selectivity over the Ag-Al_2O_3 SCR catalysts, which may have resulted in the lower NO_x conversions obtained. External selective injection of HCs will need to be administered if there is to be a notable improvement in NO_x reduction activity in the high load (i.e. high temperature) region for any engine speed.

3.5. Space velocity effect

The respective speeds of 1800, 1500 and 1200 rpm yielded corresponding gas hourly space velocities over the Ag-catalyst of 25,000, 20,000, and 15,000 h^{-1} respectively. The residence time thus increases with decreasing engine speed and may lead to increased NO_x reduction activity [23]. The SV effect is illustrated in Fig. 10, where the NO_x conversion with and without the PC over the same engine load range is shown. It was observed that the PC increased the SCR inlet temperature (by approx. 10–40 °C) in all three engine speed representations. The increase in temperature is due to the oxidative catalytic activity over the PC and the associated temperature gradient in the direction of exhaust gas flow after the catalyst [24].

At the SV of 25,000 h^{-1} (1800 rpm) the residence time between the catalyst reactive surface and the exhaust gas was shortest (compared to SV of 15,000 and 20,000 h^{-1} respectively), but increased temperatures at the high speed conditions resulted in relatively good NO_x reduction activity for temperatures above 190 °C, due to the advanced PC and Ag-Al_2O_3 light-off at these particular conditions (Fig. 10a). Due to the constant HC conversion observed over the PC prior to the Ag-Al_2O_3 SCR catalysts (Fig. 2), less SCR catalyst surface species accumulation and improved inlet temperatures were observed [24,25]. The PC initiated Ag-Al_2O_3 catalyst light off earlier than without PC use, especially at lower loads. Confirmation of this characteristic was also observed at the SV of 20,000 h^{-1}, where the PC helped maintain a NO_x conversion rate that was higher than that without the use of the PC (Fig. 10b). This lower SV may have been near optimum for the Ag-Al_2O_3 SCR catalysts used at this specific engine speed–load range. At the even lower SV of 15,000 h^{-1} (Fig. 10c), it was noticed that the PC had no significant influence on the NO_x reduction activity compared to the results with no PC use, yielding results similar to those observed at 25,000 h^{-1} whereby there was no notable improvement in NO_x reduction with PC use. Possible explanations at these particular conditions can be due to (i) the reactive reductant in the exhaust gas composition requiring either lesser or greater residence time over the SCR catalyst surface for improved NO_x reactivity or (ii) the homogeneous gas phase reactions having become significant prior the PC; reaching a point where they were much greater than the catalytic reactions over the PC and as result the PC may not have been required in the diesel exhaust system prior to the Ag-Al_2O_3 SCR catalysts [23].

4. Conclusions

The prototype oxidation catalyst has been shown to mainly reduce the hydrocarbons, carbon monoxide and particulate matter from engine exhaust gas; which in turn helps enhance low temperature NO_x reduction activity at particular operating conditions. It is suspected that at low temperatures the prototype catalyst activates the more reactive long chain HC species, which aid the NO_x reduction reaction.

At high temperatures the PC readily oxidises the PM and short chain HCs from the engine exhaust gas which when coupled with the low HC:NO_x ratios observed, leads to lower NO_x reduction activity over the Ag-Al_2O_3 catalysts. At these conditions, an external hydrocarbon injection source may be required to achieve reasonably good reactant ratios (in the presence of H_2) and thus possibly improve the NO_x reduction activity over the Ag-Al_2O_3 SCR catalysts. During the short chain HC species analysis, toluene was found to be the most abundant species after the combustion process. Due to its lack of NO_x reactivity as a reductant over Ag-Al_2O_3 catalysts, it can easily be deduced that the quality of reductant species in the exhaust gas could yield better NO_x reductions. Thus, maintaining the use of the PC and quantitatively as well as qualitatively dosing the exhaust gas may be the way forward.

Gas hourly space velocity has to be carefully controlled for the prototype oxidation catalyst to have any positive effect on passive Ag-Al_2O_3 catalyst performance for NO_x reduction. Furthermore, optimized H_2:HC and HC:NO_x ratios would be required to maximise the NO_x reduction performance of the SCR catalysts at specific conditions since it was found that the lower the HC:NO_x the lower the H_2 required for maximum possible NO_x conversion at a particular exhaust composition.

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References

[1] T. Watanabe, K. Kawashima, Y. Tagawa, K. Tashiro, H. Anoda, K. Ichioka, S. Sumiya, G. Zhang, New DOC for light duty diesel DPF system, SAE Paper No. 2007-01-1920, 2007.

[2] V.R. Lakkireddy, H. Mohammed, J.H. Johnson, The effect of a diesel oxidation catalyst and a catalyzed particulate filter on particle size distribution from a heavy duty diesel engine, SAE Paper No. 2006-01-0877, 2006.

[3] V.R. Lakkireddy, H. Mohammed, J.H. Johnson, S.T. Bagley, The effect of a diesel oxidation catalyst and a catalyzed particulate filter on the emissions from a heavy duty diesel engine, SAE Paper No. 2006-01-0875, 2006.

[4] S. Sumiya, H. Yokota, Diesel oxidation catalyst system for PM control, SAE Paper No. 2004-28-0069, 2004.

[5] J.R. Hernández Carucci, A. Kurman, H. Karhu, K. Arve, K. Eränen, J. Wärnå, T. Salmi, D.Yu. Murzin, Kinetics of the biofuels-assisted SCR of NOx over Ag/alumina-coated microchannels, Chemical Engineering Journal (2009), doi:10.1016/j. cej.2009.01.031.

[6] X. Zhang, Y. Yu, H. He, Effect of hydrogen on reaction intermediates in the selective reduction of NO_x by C_3H_6, Applied Catalysis B: Environmental 76 (2007) 241.

[7] K. Arve, H. Backman, F. Klingstedt, K. Eränen, D.Y. Murzin, Kinetic considerations of H_2 assisted hydrocarbon selective catalytic reduction of NO

over Ag/Al_2O_3. I. Kinetic behaviour, Applied Catalysis A: General 303 (2006) 96.

[8] S. Satokawa, J. Shibata, K. Shimizu, A. Satsuma, T. Hattori, T. Kojima, Promotion effect of hydrogen on lean NO_x reduction by hydrocarbons over Ag/Al_2O_3 catalyst, Chemical Engineering Science 62 (2007) 5335.

[9] Hongyi Dong, Shijin Shuai, Rulong Li, Jianxin Wang, Xiaoyan Shi, Hong He, Study of NO_x selective catalytic reduction by ethanol over Ag/Al_2O_3 catalyst on a HD diesel engine, Chemical Engineering Journal 135 (2008) 195.

[10] J.P. Breen, R. Burch, A review of the effect of the addition of hydrogen in the selective catalytic reduction of NO_x with hydrocarbons on silver catalysts, Topics in Catalysis 39 (1–2) (2006) 53.

[11] D.L. Trimm, Catalyst design for reduced coking (review), Applied Catalysis 5 (1983) 263.

[12] V. Houel, P. Millington, R. Rajaram, A. Tsolakis, Promoting functions of H_2 in diesel-SCR over silver catalysts, Applied Catalysis B: Environmental 77 (2007) 29.

[13] D. Creaser, H. Kannisto, J. Sjöblom, H.H. Ingelsten, Kinetic modelling of selective catalytic reduction of NO_x with octane over $Ag\text{-}Al_2O_3$, Applied Catalysis B: Environmental 90 (2009) 18.

[14] A. Tsolakis, A. Megaritis, M.L. Wyszynski, Application of exhaust gas fuel reforming in compression ignition engines fueled by diesel and biodiesel fuel mixtures, Energy & Fuels 17 (2003) 1464.

[15] A. Tsolakis, A. Megaritis, Exhaust gas fuel reforming for diesel engines—a way to reduce smoke and NO_x emissions simultaneously, SAE Paper No. 2004-01-1844, 2004.

[16] K. Arve, F. Klingstedt, K. Eränen, L.-E. Lindfors, D.Y. Murzin, HC-SC.R. Engineering, Improved low temperature performance through a cascade concept, Catalysis Letters 105 (3–4) (2005) 133.

[17] J.P. Breen, R. Burch, C. Hardacre, C.J. Hill, B. Krutzsch, B. Bandl-Konrad, E. Jobson, L. Cider, P.G. Blakeman, L.J. Peace, M.V. Twigg, M. Preis, M. Gottschling, An investigation of the thermal stability and sulphur tolerance of $Ag/\gamma\text{-}Al_2O_3$ catalysts for the SCR of NO_x with hydrocarbons and hydrogen, Applied Catalysis B: Environmental 70 (2007) 36.

[18] S. Sitshebo, A. Tsolakis, K. Theinnoi, Promoting hydrocarbon-SCR of NO_x in diesel engine exhaust by H_2 and fuel reforming, International Journal of Hydrogen Energy 34 (2009) 7842.

[19] K. Eränen, L.E. Lindfors, A. Niemi, Influence of hydrocarbons on the selective catalytic reduction of NO_x over Ag/Al_2O_3—laboratory and engine tests, SAE Paper No. 2000-01-2813, 2000.

[20] K. Theinnoi, S. Sitshebo, V. Houel, R. Rajaram, A. Tsolakis, Hydrogen promotion of low-temperature passive hydrocarbon-SCR over a silver catalyst, Energy & Fuels 22 (6) (2008) 4109.

[21] K. Eränen, F. Klingstedt, K. Arve, L.E. Lindfors, D.Y. Murzin, On the mechanism of the selective catalytic reduction of NO with higher hydrocarbons over a silver/alumina catalyst, Journal of Catalysis 227 (2004) 328.

[22] K. Arve, F. Klingstedt, K. Eränen, J. Wärnå, L.-E. Lindfors, D.Yu. Murzin, Kinetics of NO_x reduction over Ag/alumina by higher hydrocarbon in excess of oxygen, Chemical Engineering Journal 107 (2005) 215.

[23] K.M. Adams, J.V. Cavataio, R.H. Hammerle, Lean NO_x catalysis for diesel passenger cars: investigating effects of sulfur dioxide and space velocity, Applied Catalysis B: Environmental 10 (1996) 157.

[24] R.E. Hayes, S.T. Kolaczkowski, Introduction to Catalytic Combustion, Gordon and Breach Science Publishers, 1998 (ISBN 90-5699-092-6).

[25] K. Nagashima, Y. Banno, Y. Kanno, M. Nagata, SOF combustion behaviour in flow-through diesel oxidation catalysts, SAE Paper No. 2004-01-1942, 2004.