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Efficient low temperature lean NO_x reduction over Ag/Al_2O_3 – A system approach

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Abstract

This study focuses on lean NO_x reduction (LNR) by *n*-octane using silver-alumina based catalysts, with the addition of hydrogen. The work takes a system approach, where parameters such as temperature, reformate gas composition, fuel penalty and realistic monolith samples are considered. The LNR catalyst samples were prepared by impregnation and sol-gel methods and the NO_x reduction performance was characterized by flow-reactor experiments, where realistic engine-out gas compositions were used. The hydrogen feed over the LNR catalyst samples was determined via data achieved by autothermal reforming experiments over a rhodium based catalyst, using real diesel as feedstock. The LNR catalyst samples generally show an enhanced NO_x reduction when hydrogen is added to the gas feed. In particular, a 2 wt% silver-alumina sample with the addition of minute amounts of platinum, shows a high increase in NO_x reduction when hydrogen is added to the feed. The addition of CO, a potential poison in the reaction and a by-product from the reforming, did not show any significant effect on the LNR catalyst performance at the conditions used. This is beneficial, since it renders a CO clean-up step in the reformer system unneeded. Ammonia formation is discussed in terms of a possible dual-SCR system. Finally, the fuel penalty for hydrogen production and hydrocarbon addition is taken into consideration. It is found that an addition of 1000 ppm H_2 leads to unacceptable fuel penalties.

Keywords: Lean NO_x reduction, Ag/Al_2O_3, Pt, fuel reforming, fuel economy.

1. Introduction

Combustion in excess oxygen, as in diesel- and lean-burn engines, can significantly improve the fuel economy for automotive engines, thus reducing the formation of CO_2. However, the lean environment in the exhaust gas obstructs the ability of the conventional three-way catalyst to reduce NO_x. New strategies for efficient lean NO_x reduction must therefore be developed. In connection to this, fuel cell auxiliary power (FC-APU) and hydrocarbon selective catalytic reduction (HC-SCR or LNR) units are proposed as two major strategies as ground for introducing hydrogen in the transport sector to reduce emissions.

A promising catalyst for HC-SCR is silver-alumina [1-7], over which high conversion of NO_x to N_2 with hydrocarbons as reductant has been demonstrated [2, 7-13]. However, poor performance at low temperatures, typically 150–300 ^{o}C, is a drawback since efficient NO_x abatement at these temperatures is required for *e.g.* diesel engine exhausts. By using long-chained hydrocarbons the SCR reaction has previously been shown to proceed at lower temperatures and with wider activity window, compared to using shorter hydrocarbons [11, 14, 15]. The reason for this effect is suggested to be related to the lower activation (*i.e.* partial oxidation) temperature for longer hydrocarbons, compared to shorter ones [15, 16]. Furthermore, results show that the addition of small amounts of hydrogen drastically improves the low-temperature activity, first reported by Satokawa [17] in 2000.

On-board fuel processing of liquid hydrocarbon fuels is a way to supply hydrogen to a vehicle by using the existing fuel infra-structure. The hydrogen can be used either for avoiding operation of a truck engine at stand-still by using an APU system, or to increase the low-temperature activity

of silver-based NO_x reduction catalysts. The latter option will be discussed in this paper. An FC-APU system could also be used in marine applications or as a range extender in a fuel cell vehicle. The critical step in the reforming process is the evaporation and catalytic conversion of the hydrocarbon fuel into a hydrogen-rich reformate. Rh-based monolithic catalysts have proven to be very active for autothermal reforming (ATR) of diesel [18]. Furthermore, these catalysts have showed a high selectivity and a good durability while using commercial diesel fuels.

Limited number of studies can be found in the open literature where the performance of a HC-SCR catalyst has been investigated using both diesel reformate and exhaust gas as feedstocks [19, 20]. Along with hydrogen production also carbon monoxide is formed in the reformer system. For use in e.g. a polymer electrolyte fuel cell (PEFC) based APU system, high CO levels (>10 ppm) is a major drawback since it poisons the electrodes in the fuel cell [21]. In the NO_x reduction, however, the effect of CO is not necessarily negative. Furthermore, production of hydrogen in a fuel reformer causes a fuel penalty, which, together with the need for a reducing agent in the LNR unit (*i.e.* fuel), should be minimized in order to maintain high fuel economy. Many studies in the literature reports on the effect of hydrogen on the NO_x reduction over the silver-alumina system, and often the hydrogen concentration is high (ranging between 1000 ppm and 1 vol%) [22]. One possible side effect of hydrogen addition to the silver-alumina catalyst is the formation of ammonia, which is mainly considered as negative, as ammonia is harmful for the environment. However, attempts have been made in order to use the formed ammonia in a NH_3-SCR catalyst after the HC-SCR catalyst. The concept has been shown by DiMaggio et al. [23], where remaining NO_x species are reduced by the ammonia formed over the HC-SCR catalyst.

The aim of the present study is to investigate how various parameters, such as hydrogen and carbon monoxide concentration, affects the NO_x reduction over the silver-alumina system. This work takes a system approach where parameters as temperature and fuel penalty are considered. Furthermore, realistic gas mixtures from exhaust and reformer are used in the experiments and the catalysts are coated on monolith samples to mimic a real system.

2. Experimental

2.1 ATR catalyst preparation

Table 1 shows the washcoat properties of the support and the RhPt-based catalyst used for the ATR experiments. The metal precursors used for the catalyst preparation were Rh nitrate ($Rh(NO_3)_3$, Rh 8-10 % w/w, Sigma Aldrich), Pt nitrate ($(NH_3)_4Pt(NO_3)_2$, Pt 3-4 % w/w, Alfa Aesar), Ce nitrate ($Ce(NO_3)_3{\cdot}6H_2O$, 99.99 %, Alfa Aesar)) and La nitrate ($La(NO_3)_3{\cdot}6H_2O$, 99.9 %, Alfa Aesar) solutions. The catalyst was supported on δ-alumina. The δ-alumina was made by calcining γ-alumina (PURALOX HP-14/150, Sasol Germany GmbH) at 1000 ºC for 1 h with little loss of surface area. The alumina powder was impregnated with the metals by the incipient wetness (IW) technique in accordance to the nominal weight loading presented in Table 1. The resulting powders were calcined at 800 ºC for 3 h and deposited via ethanol-slurry dip-coating procedure onto 400 cpsi cordierite monoliths, with dimensions OD=17.8 mm, l=30.5 mm (Corning).

2.2 ATR catalyst characterization

Fresh powder samples of $Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta\text{-}Al_2O_3$, taken from the catalyst preparation prior to the deposition on the monoliths, were characterized by using the following instruments: Surface area and pore size distribution were measured by nitrogen sorption at 77K using a Micromeritics

ASAP 2010 instrument. Approximately 0.4 g powder was used and degassed at 250°C for 3 h prior to analysis.

The crystal phases were determined by X-ray diffraction (XRD), using a Siemens Diffraktometer D5000 scanning 2θ from 10º-90º in the scan mode (0.02º, 1s), using Ni filtered Cu-Kα radiation. Temperature programme reduction (TPR) was performed at 30-1000°C, 10°C/min, with hydrogen as adsorbate using a Micromeritics Autochem 2910 equipped with a TCD. Approximately 0.1 g powder was used for the analysis.

The surface composition and chemical state of the deposited additives and loaded active metals were determined using X-ray photoelectron spectroscopy (XPS). The XPS studies were performed in a Phi Quantum 2000 system.

2.3 ATR experiments

The diesel reforming experiments were carried out at reactor inlet temperature of 650 ºC and atmospheric pressure. A standard diesel fuel (~C/H=6.43 (weight ratio), ~6 ppm S,) whose physical and chemical properties are in close correlation to Swedish Environmental Class 1 diesel (MK 1) [24], was used as feedstock. The following operating parameters were employed: $H_2O/C=3.0$, $O_2=0.49$ ($\lambda=0.33$), GHSV~17700 h^{-1} and time on stream (TOS) ~3h. The experiments were carried out in a vertically mounted stainless steel tubular reactor with ID=23.7 mm equipped with three thermocouples. The product gases were analyzed using a Gasmet Cr-200 Fourier Transform Infrared Spectroscopy (FTIR) and a Maihak modular system S710 equipped with non-dispersive infrared sensor (NDIR) and thermal conductivity detector (TCD).

2.4 LNR sample preparation

The LNR catalyst samples were prepared via wet impregnation and two single step sol-gel methods, as described previously [25]. The wet impregnation was performed by adding an Ag/EDTA-complex solution to a water based γ-Al_2O_3 slurry (SBa200, Sasol), which was kept under stirring for 2 hours ($AgNO_3$ (≥99%, Sigma-Aldrich) as precursor) while the pH was kept at 6.3 by nitric acid (10 %, Fluka) addition. The slurry was subsequently freeze-dried and calcined at 600°C. In the sol-gel methods, aluminum isopropoxide (AIP; 98+%, Aldrich) and silver nitrate were used as precursors. The formed gel was subsequently dried (thermally at 100 °C or by freeze-drying) followed by calcination at 600°C, and was then crushed to a fine powder. All samples were washcoated onto monoliths (400 cpsi, length 20 mm, 21 mm OD), using 20 wt% boehmite as binder. Further details about the preparation methods and the washcoating have been presented previously [25].

To activate the hydrocarbon for NO_x reduction in the SCR reaction, it is necessary to partially oxidize the hydrocarbon [12]. Platinum is a known oxidation catalyst, and can thus act as oxidation sites on the catalyst. However, the oxidation must be mild enough not to combust the reductant, but high enough to partially oxidize the hydrocarbon, preferably at low temperatures (below 300 °C). To achieve these properties of the catalyst, a minute amount of Pt (100 ppm by weight) was added to a catalyst containing 2 wt% Ag (nominal) prepared by sol-gel with freeze-drying. The platinum was added as a diluted (1000 ppm Pt by weight) platinum nitrate solution to the sol, one hour before gelling. Sol-gel with subsequent freeze-drying has been shown to highly distribute the metal throughout the alumina matrix [25], which is believed to promote the desired properties of the catalyst.

The specific surface areas of the samples were measured by nitrogen sorption at 77 K, using a Micromeritics Tristar instrument. The results are summarized in Table 2, together with the nominal metal content. The samples were denominated according to Table 2.

A thorough characterization of the different LNR catalyst samples was performed in ref. [25]. The amount of Pt in the Pt containing sample (2%AgPt100) was too low to be detected by the techniques applied in ref. [25]. Nevertheless, this sample showed similar characteristics as the corresponding silver-alumina sample without Pt addition.

2.5 LNR performance

Two similar flow reactor systems were used for evaluation of the catalytic performance of the samples. The reactors consisted of a horizontal quartz tube heated by a heating coil, where the temperature was measured by two thermocouples (type K), 15 mm before the sample and inside the monolith sample (just before the rear end), respectively. Two uncoated 400 CPSI cordierite monoliths were placed before and after the sample monolith, respectively, to screen the thermocouples from radiation from the heating coil (first monolith) and to prevent heat losses via radiation from the back of the sample monolith (second monolith). The inlet gas composition was controlled by mass flow controllers from Bronkhorst High-Tech. Both reactors outlet gas composition was analyzed by an MKS 2000 FTIR instrument. *n*-octane and water were introduced separately to the reactors via controlled evaporator mixer (CEM) systems from Bronkhorst High-Tech. Overall, the differences between the reactor systems were negligible.

The samples were pre-oxidized in 10% O_2 (Ar bal.) at 550°C for 20 minutes prior to the measurements. The measurements were carried out at steady state conditions at 200 °C, 250 °C

and 300 °C with a space velocity (GHSV) corresponding to 33 300 h^{-1}. The inlet gas composition was set to 200 ppm NO, 5% H_2O, 6% CO_2 and 10% O_2 (Ar bal.). To monitor the influence of the addition of reformate gas to the feed, the CO and H_2 concentrations were varied. The H_2 concentration was varied between 0 and 1000 ppm, while the CO concentration was varied between 350 and 850 ppm. At 250 °C, additional H_2 and CO concentrations of 3000 ppm and 1850 ppm, respectively, were also introduced. This was to simulate different reformate gas feeds and to investigate the need for an on-board CO clean-up equipment. *n*-octane was used as reducing agent and the C/N ratio was varied between 3 and 12. At 250 °C an additional C/N ratio of 8 was included in order to investigate the influence of the C/N ratio at low temperatures in more detail.

For some runs, an error in the program controlling the MFCs caused a faulty argon balance, leading to a somewhat decreased concentration of the inlet gases. This error mainly affected the NO, CO and H_2 concentration and the overall space velocity, especially for the cases with 3000 ppm H_2 in the feed. However, the molar flow of all gases (except argon) remained constant. The conversion of NO_x was therefore calculated from the real inlet concentration for the affected cases. The increase in space velocity was always less than 7.5 % and thereby considered to have a minor effect on the NO_x conversion. This increase in space velocity was therefore neglected in the calculations. Based on the calculated results it was concluded that the erroneous argon balance did not significantly affect the discussion and conclusions of this study.

3. Results

3.1 ATR catalyst characterization results

The surface area and porosity results from the N_2-BET measurements of the $Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta$-$Al_2O_3$ sample are presented in Table 1. As seen in Table 1, the addition of the active metal and promoters reduced the surface area, the pore volume and the pore diameter of the δ-alumina support. The surface area of the thermal treated δ-alumina was ~105 m^2/g while for the impregnated RhPt-sample it was 88 m^2/g.

The XRD pattern of the catalyst showed that the δ-phase of alumina was present for the fresh powder sample. Furthermore, only diffraction peaks from ceria and the support material were observed. This indicates that the rhodium and platinum particles are small and well dispersed in the washcoat. Peaks ascribed to fluorite-structured CeO_2 [26] were found at 2θ= 28.5, 48.5 and 56.5º. The average crystallite size of ceria was ~8.0 nm.

The TPR profile of $Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta$-$Al_2O_3$ revealed three positive peaks. One major peak located at 150 ºC, while the other was smaller and found at 450 and 900 ºC, respectively. The reduction peak present at 150 ºC is ascribed to reduction of bulk rhodium oxides species Rh_xO_x [27], the peak at 450 ºC is owing to hydrogen spillover effect in the alumina support [27], while the peak at 900 ºC is attributed to cerium oxides [28]. Platinum and lanthanum oxides were not detected by TPR.

XPS measurements provided valuable information of the surface composition and oxidation state of the fresh catalyst (Table 3). Rhodium was found to be present in its oxidized state with a binding energy of 308.8 eV [29]. For platinum, the Pt(4d) peaks occur at about 314.0 eV which is metallic [29]. For ceria, the binding energy of the Ce $3d_{5/2}$ line is found at 881.8 eV, indicating

CeO_2 [29]. The XPS survey spectra shows that La(3d) peaks is found at ~834.2 eV with a La/Al ratio of 0.091 indicating that La is in the dispersed phase [30].

3.2 ATR catalyst performance.

The performance of the catalyst using standard diesel as feedstock at reaction conditions H_2O/C~3.0 and O_2/C~0.49 are presented in Table 4. The activity results show that the washcoated monolith with the composition $Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta\text{-}Al_2O_3$ is capable of providing a high diesel conversion, ~99%. The CO_2 selectivity expressed as the ratio $CO_2/(CO_2+CO)$ was also high, just above 50%. The hydrogen concentration was 36 %. The measured hydrocarbon concentrations in the reformate were low. The methane concentration was ~600 ppm, while the ethylene concentration was ~300 ppm. No ethane, propane nor higher hydrocarbons were detected in the product gas. Also, very low amounts (total <10 ppm) of benzene, toluene and sulfur dioxide were detected by the FTIR and NDIR measurements.

The activity results from the $Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta\text{-}Al_2O_3$ were used as a basis for the $deNO_x$ experiments, which are discussed in detail in the following sections.

3.3 LNR performance - Influence of feed composition

3.3.1 Influence of C/N ratio and CO feed concentrations

The LNR performance for the catalyst samples, in the absence of hydrogen, was evaluated at 200, 250 and 300 °C with the C/N ratios of 3 and 12, respectively, and different CO inlet concentrations (350 or 850 ppm). It is clear that without the addition of hydrogen no significant activity was observed below 300 °C, except for a slight NOx conversion (<5 %) for the high load (5%Ag and Mix) samples at 250 °C and C/N=12. At 300 °C however, most samples clearly show

the reduction of NO_x (2%AgPt100 excepted). In general, the CO concentration did not show any promotional influence on the NO_x conversion, regardless of temperature, in accordance to the results of e.g. Bogdanchikova et al. [31] and Breen et al. [32]. Overall, the results showed no significant effect of the CO concentration in the feed. Without the addition of hydrogen in the NO_x conversion experiments, differences owing to the C/N ratio were hardly observable at temperatures below 300 °C and then only for the high load samples. Nevertheless, at 300 °C the increase in NO_x conversion for these samples were considerable, from 13 % to ca 46 % (5%Ag) and from ca 15 % to ca 55 % (Mix), at C/N=3 and 12, respectively. The low loaded samples (2%Ag and 2%AgPt100) did not show any significant increase in NO_x conversion due to changes in the C/N ratio at 300 °C: The 2%Ag sample showed a NO_x conversion of about 16 %, while the 2%AgPt100 sample always showed less than 10 % NO_x conversion at these conditions.

3.3.2 Addition of hydrogen

The addition of 1000 ppm of hydrogen to the feed (Figure 1) results in an instant increase in NO_x conversion, as frequently reported in the literature since the work of Satokawa [17]. The effect of the added hydrogen is clearly dependent on the temperature, as the difference in NO_x conversions with and without hydrogen added is generally larger at higher temperatures. However, evaluating the individual results for the samples, there are exceptions: For C/N=3 and 250 °C, the high load samples show a slightly lower NO_x conversion with H_2 in the feed than at 200 °C. Nevertheless, the differences are small and fall within experimental errors. For C/N=3, the largest difference in NO_x conversion owing to H_2 addition is shown by the 2%Ag sample at 300 °C, increasing from around 17 % to 61 %. For C/N=12 however, the largest differences are shown for the Mix sample at 250 °C, increasing from ca 8 % to 74 %, but also (and more notably) for the 2%AgPt100 sample at 300 °C, increasing from around 7 % to almost 88 %, a more than 12-fold increase in

NO_x conversion. At 300 °C, it is observed that the 2%Ag sample does not seem to be affected by the change in C/N ratio, while on the other hand it has a considerable impact on the 2%AgPt100 sample.

3.3.3 Influence of hydrogen feed concentration

According to the results in Figure 1, the lowest temperature showing any significant NO_x conversion is 250 °C, with C/N=12. To increase the NO_x conversion at this temperature within the limits of the reformer, 3000 ppm of hydrogen was added to the feed. Also, an additional intermediate C/N ratio of 8 was added to investigate the possibility of somewhat lowering the fuel penalty while maintaining a high NO_x conversion. The CO feed was accordingly varied between 350 ppm and 1850 ppm, simulating a reforming system with and without CO clean-up. The results are shown in Figure 2.

At C/N=3 with 350 ppm CO and 3000 ppm H_2, the high load samples show a slight increase in NO_x conversion, from about 18 % to ca 24 % for both samples, compared to 1000 ppm H_2 and 350 ppm CO in the feed (Table 6). The 2%Ag and 2%AgPt100 samples show a somewhat larger increase in NO_x conversion from 18 % or 21 % with 1000 ppm H_2, to 32 % and 38 %, respectively, with 3000 ppm H_2 in the feed. It is observed that the low load samples both show higher NO_x conversion than the high load samples at these conditions. The increase of the CO feed concentration from 350 ppm to 1850 ppm (Figure 2) seems to have a slightly positive effect on the overall NO_x conversion at these conditions, showing an increase with approximately 3-6 percentage units for all samples.

For C/N=12 at 250 °C, the increase in hydrogen concentration results in a significant increase in NO_x conversion for all samples, comparable with the results at 300 °C with 1000 ppm H_2 in the

feed (Figure 1, top right). In contrast to C/N=3, the CO feed concentration does not affect the NO_x conversion at C/N=12 in any other significant way but slightly negative (Figure 2). Comparing C/N=12 and C/N=8 (Figure 2) with 350 ppm CO, the NO_x conversion drops from 82 % to 61 % for the 5%Ag sample and from 91 % to 67 % for the Mix sample. However, for the 2%Ag sample the drop in NO_x conversion is smaller, from 64 % to 57 %, and for the 2%AgPt100 the drop is merely five percentage units, from 80 % to 75 %. Increasing the CO feed concentration at C/N=8 have no significant effect on the 2%Ag and 2%AgPt100 samples, however, a slight promotion of the NO_x conversion over the 5%Ag (61 % vs. 66 %) and Mix (67 % vs. 71 %) samples is observed.

3.4 NH_3 formation

The formation of nitrogen containing species, such as isocyanate, isocyanide and ammonia, during the HC-SCR reaction is well known and has been extensively reported [23, 33-38] and hydrogen has been shown to promote the formation of such species [23, 33, 34, 36, 38]. In this study, we observe the formation of ammonia (Table 5), especially with the addition of hydrogen to the feed (Figure 3), in accordance with the literature.

The ammonia is formed during the HC-SCR reaction under certain conditions. According to the results presented in Table 5, where no hydrogen is added to the feed, the only significant formation of ammonia is observed for the high load samples at 300 °C and a C/N ratio of 12. Notably, the amount of ammonia formed corresponds to about 20-25 % of the converted NO_x at these conditions. A small amount of formed ammonia is also observed at 200 °C for these samples. However, considering the low NO_x conversion at these conditions, these results should be regarded as possible artifacts, based on the fact that the formed ammonia would, in that case,

correspond to almost 100 % of the converted NO_x, which is highly unlikely. On the other hand, we were not able to directly measure the formation of N_2 during the experiments, while it is not possible to entirely rule out this scenario. Figure 3 show the ammonia formation over the catalytic samples at different temperatures and C/N ratios when 1000 ppm hydrogen is added to the feed. At C/N=3 the formation of ammonia is very low, regardless of temperature, despite a NO_x conversion between 30 % and 60 % for the different samples at 300 °C. At C/N=12 however, a significant formation of ammonia can be observed over the high loaded samples at all temperatures, especially at 300 °C with over 50 ppm of formed ammonia over both samples. Most notable is the formation of ammonia over the high load samples at 200 °C, occurring at a NO_x conversion of 21 % (5%Ag) and 26 % (Mix). The low loaded samples show a low ammonia formation overall, also for the high C/N ratio of 12. Only at 300 °C the 2%AgPt100 sample show any significant formation of ammonia (~14 ppm), while the ammonia formation over the 2%Ag sample never exceeds 10 ppm.

Figure 4 shows the ammonia formation at 250 °C with 3000 ppm H_2 added to the feed, also including the additional C/N ratio of 8. The low loaded samples still show a very low formation of ammonia at all conditions. The high loaded samples on the other hand, show an increase in NH_3 formation in comparison to 1000 ppm H_2 in the feed and C/N=12 (Figure 3, middle right). A slight increase is also shown at C/N=3 for these samples. At C/N=8 and 3000 ppm H_2, the 5%Ag sample actually shows a slight increase in NH_3 formation compared to C/N=12 with 1000 ppm H_2 in the feed, while the Mix samples show almost the same NH_3 formation comparing the same conditions. From the results in Figure 3 and Figure 4 we cannot observe any impact owing to the CO concentration regarding the ammonia formation. Not even the considerable increase from 350

ppm to 1850 ppm CO when adding 3000 ppm H_2 to the feed shows any significant effect on the NH_3 formation.

3.4.1 Dual SCR system

One possible way to make use of the formed ammonia is to add a NH_3-SCR catalyst after the HC-SCR catalyst. The concept has been shown by DiMaggio et al. [23], where remaining NO_x species are reduced by the ammonia formed over the HC-SCR catalyst. To investigate the impact of such a system, we calculated the total NO_x reduction according to the following assumptions:

1. All NO in the gas feed that is converted over the HC-SCR catalyst forms either N_2 or NH_3.
2. All ammonia that is formed over the HC-SCR catalyst is available as reducing agent for the NO reduction over the NH_3-SCR catalyst, in the ratio 1:1.

The results are presented in Table 6.

4. Discussion

4.1 Fuel reforming

The activity results (Table 4) at ATR reaction conditions $H_2O/C \sim 3.0$ and $O_2/C \sim 0.49$ show that the $Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta\text{-}Al_2O_3$ catalyst is highly active and capable of catalytically reforming the molecules in the diesel fuel to obtain close to complete fuel conversion. This feature is positive as a good fuel economy is crucial for diesel trucks, (see also section 4.4). Fuel slip from the reformer can deactivate the fuel cell e.g. in a polymer electrolyte fuel cell (PEFC) based APU system. The long hydrocarbon chains in diesel can easily get attached in the pores of the membranes, hindering the transport of the hydrogen ions from the anode to the cathode side [39].

Fuel slip does not have a negative effect on the LNR performance. The high hydrogen concentration, ~36 vol%, noted in Table 4, is more than sufficient to provide both the PEFC and LNR units with enough H_2 for power generation and NO_x reduction. In Table 4, the high CO_2 selectivity, ~52%, is also positive as high CO concentrations are known to deactivate PEFCs due to CO adsorption on the typically Pt-coated anode electrodes [21]. However, for the LNR unit our results show that CO has no significant effect on the NO_x reduction performance. The activity results in Table 4 show that low methane and ethylene concentrations, 600 and 300 ppm, respectively, were detected in the reformate by the FTIR and NDIR units. In reforming, generating low level of ethylene concentration in the reformate is considered crucial as ethylene is a known coke precursor. A high ethylene concentration is often an indication of severe carbon deposition taking place on the catalyst [40, 41]. This is detrimental as this often leads to significant reduction of the diesel reforming catalyst long term performance as the active surface sites of the catalyst are blocked by various types of carbon deposits. Further, these short hydrocarbons are generally not active over Ag/Al_2O_3 at the current temperatures [15], while a clean-up catalyst after the LNR unit is required to prevent HC-slip.

The characterization results from the N_2-BET, XRD, H_2-TPR and XPS analyses (Table 1 and 3) show the presence of finely dispersed bulk rhodium oxides, metallic platinum, ceria and lanthanum on the delta phase generated alumina support. These states of the active metals and promoters are believed to improve the catalyst reforming activity, stability and durability. The effects of the Rh-Pt metal loading and the addition of Ce-La additives on delta alumina were studied and reported in previous work [42, 43]**.** It was noted that the amount of accessible rhodium oxides and the introduction of ceria and lanthana on the alumina support were crucial as these features had a significant positive effect on the X_{diesel}, S_{CO2} and H_2 formation during ATR

of diesel at reaction conditions $H_2O/C\sim2.5$ and $O_2/C\sim0.49$ [42, 43]**.** Furthermore, it was found that ceria-rhodium and ceria-platinum interactions enhanced the development of bulk RhO_x species which was believed to improve the catalyst activity, in particular the fuel conversion. Also, ceria was found to reduce the ethylene concentration in the reformate.

4.2 NO_x conversion

The results without the addition of hydrogen show that the high load (5%Ag and Mix) samples have a significantly higher NO_x conversion than the low load (2%Ag and 2%AgPt100) samples at 300 °C and C/N=12. This higher activity is visible also at 250 °C and C/N=12 for the same samples, however to a lesser degree than at 300 °C. Most notable though is the 2%Ag sample that shows a higher NO_x conversion at 300 °C and C/N=3 (16 %) than both high load samples (14 %), let be that the differences are small. The activity then slightly decreases when the C/N ratio is increased. This implies that the surface of the 2%Ag sample is at least partially covered by the *n*-octane, blocking the active sites. This has been shown by e.g. Shimizu et al. [15]. The higher activity shown by the high load samples is attributed to the higher amount of oxidation sites (metallic silver particles) in the samples, according to results from a previous study by Kannisto et al. [25]. The higher number of oxidation sites on the sample surface can readily oxidize and/or partially oxidize the high amount of octane at C/N=12 and 300 °C, which is crucial for a high NO_x conversion. At C/N=3 and 300 °C, the high number of oxidation sites may lead to combustion of the octane, decreasing the NO_x conversion. In this case (C/N=3), the lower amount of oxidation sites in the 2%Ag sample can partially oxidize a higher fraction of the hydrocarbon, avoiding combustion, than the high loaded samples, which is also showed in the higher NO_x conversion.

Adding 1000 ppm hydrogen to the feed results in an overall increase in NO_x conversion (Figure 1), but more importantly the results confirm the previous conclusions. At C/N=3 the overall NO_x conversion is low at temperatures below 300 °C. At 300 °C though, the NO_x conversion is increased with the 2%Ag sample again showing the highest activity. At C/N=12 the activity increases already above 200 °C, with the high load samples showing the highest NOx conversion. However, the 2%AgPt100 sample now shows an increased NO_x conversion, especially at 300 °C, where it is comparable with the conversion of the high load samples, around 90 %. These results imply that the platinum dopant acts as an oxidation site able to partially oxidize the hydrocarbons, as discussed above. The lack of activity without the addition of hydrogen may be due to that the platinum most likely is in an oxidized state during these experiments: The samples were calcined in air and also pre-treated in 10 % oxygen at 500 °C for 20 minutes prior to each activity test. It is possible that the hydrocarbon reductant is not capable of reducing any oxidized platinum in the catalyst, while the addition of hydrogen, being a more reductive element, results in the formation of metallic platinum particles acting as oxidation sites. The low activity at C/N=3, 300 °C should then be due to combustion of the reductant, however due to the amount of CO_2 in the feed we were unable to distinguish the amount of formed CO_2 from this combustion.

Increasing the hydrogen feed to 3000 ppm at 250 °C results in even higher overall NO_x conversion. Also, the differences in activity between the samples are decreased. However, similar trends as previously are observed, with the low loaded samples showing slightly higher activity than the high loaded samples at C/N=3. However, at C/N=8 and 12, the 2%Ag sample is showing the lowest NO_x conversion, while the 2%AgPt100 sample shows similar activity as the high loaded samples, especially at C/N=8. There is a possibility that some NO_x conversion over the 2%AgPt100 sample may be due to H_2-SCR over the platinum sites [44]. However, since the NO_x

conversion increases with the C/N ratio, we draw the conclusion that the HC-SCR reaction constitutes the dominating part of the NO_x conversion for the 2%AgPt100 sample. Also, any significant effect from the H_2-SCR would have shown at 200 °C, which is not the case.

The most important conclusion from this discussion is that to achieve an efficient HC-SCR catalyst, oxidation sites that can partially oxidize the reductant is required, as previously shown in the literature for pure Ag/Al_2O_3 catalysts [12]. The results in the present study strongly imply that this can be achieved with other oxidation sites than silver, such as well dispersed trace amounts of platinum. Too great a number of oxidation sites will nevertheless naturally lead to combustion of the hydrocarbon reducing agent.

4.3 NH_3 formation

Regarding the formation of ammonia, several obvious conclusions can be drawn from the results presented in Table 5, Figure 3 and Figure 4. First, the silver loading is crucial for the formation of NH_3, as the low loaded samples show very low formation of NH_3, virtually regardless of conditions. Both samples show less than 10 ppm of ammonia at all times, except for the 2%AgPt100 sample at C/N=12 and 300 °C, showing an ammonia formation of about 14 ppm. The high load samples on the other hand, show a more significant NH_3 formation at C/N=12 and with addition of 1000 ppm H_2 (Figure 3), but also without H_2 addition at 300 °C (Table 5). Further, at C/N=8 and 12 with 3000 ppm H_2 (Figure 4) a notable amount of NH_3 is formed. Based on these results it seems as larger silver particles, present in the high load samples according to ref. [25], promote the formation of ammonia during the HC-SCR reaction. Notably, the formation of ammonia is not necessarily coupled to the NO_x conversion. As an example, the NO_x conversion is high over the low loaded samples at C/N=8 and 12, adding 3000 ppm H_2 to

the feed (Figure 2). However, the corresponding NH_3 formation is low (Figure 4), in comparison to the results of the high load samples. These results imply that the NH_3 formation does not occur over the same sites as the NO_x reduction to N_2. Also, the results strongly imply that a surplus of hydrocarbons is needed to achieve ammonia formation during the HC-SCR reaction. This is clearly shown in Figure 3 and Figure 4, as the formation of NH_3 at C/N=3 is very low over all samples and at all conditions. Hydrogen addition and increased temperatures positively influence the NH_3 formation, but the effect is only significant at high C/N ratios. This is consistent with the mechanisms for HC-SCR suggested in the literature. Eränen et al. [45] reported that ammonia is formed via isocyanate and isocyanide species. The formation of these species is promoted by the addition of hydrogen [36]. Conditions promoting a high formation of these isocyanate and isocyanide species, i.e. a high C/N ratio, addition of hydrogen and/or increased temperature, should be favourable for NH_3 formation as shown by the results in the present study.

4.3.1 Dual SCR

The NH_3 formation results confirm the findings of DiMaggio et al. [23], that hydrogen plays a crucial role in the formation of ammonia, although the experiments in the present study was conducted at a lower temperature and hydrogen concentration than in ref. [23]. Further, the results calculated for our theoretical dual SCR system show that such a system could significantly increase the NO_x reduction efficiency compared to the HC-SCR system, showing a NO_x reduction of ca 85 % for the Mix sample at 250 °C and C/N=12, provided that the assumptions stated for the calculation hold. Likely, all NO is not converted to N_2 or NH_3, but also to other nitrogen-containing species such as NO_2, amines etc. In addition, for a commercial version of such a system, diesel would be used as reductant instead of *n*-octane, further reducing the

efficiency. However, the concept of a dual SCR is shown to be promising as a way of increasing the efficiency of the HC-SCR system.

4.4 Fuel penalty

In order to maintain a good fuel economy for the diesel engine it is important to minimize the fuel penalty for the NO_x abatement. The NO_x conversion efficiency of a HC-SCR system depends on the amount of diesel that is needed to meet the conversion requirements. In general, a large HC/NO_x ratio leads to a high NO_x conversion efficiency. The results presented in this work, and in previous work (e.g. [23]), indicate that HC/NO_x ratio between 6 and 8 is sufficient for a high NO_x conversion. This will lead to a fuel penalty of about 1.8 gram of diesel for each gram of NO_x removed from the exhausts. However, in order to reach high LNR efficiency at low temperatures hydrogen needs to be added. In the present study different hydrogen concentrations have been used and about 1000 ppm of H_2 is a reasonable number in this respect. In the literature there are examples of studies where hydrogen concentrations up to 1 vol% (10 000 ppm) have been used, which would lead to unacceptable fuel penalties if utilized in real systems. A H_2 addition of 1000 ppm would correspond to approximately 2 grams of diesel fuel. The total fuel penalty is therefore 3.8 grams of diesel for each gram of NO_x removed from the system. If the fuel consumption and NO_x exhaust levels are assumed to be 200 g/kWh and 1 g/kWh, respectively, this is equivalent to a fuel penalty of about 2%.

For comparison, to reduce 1 gram of NO_x using urea-SCR, which is the presently most efficient way to remove NO_x in lean exhausts, 2 grams of urea-solution is required. The cost of urea is approximately half of the diesel cost (in Europe), which means that 1 gram of NO_x reduction is equivalent to 1 gram of diesel fuel, and a fuel penalty of approximately 0.5%. Nevertheless, as

shown earlier in this study, a dual-SCR approach may lower the fuel penalty. However, further studies to optimize such a system are needed.

5. Conclusions

This paper reports on high activity for lean NO_x reduction, already at low temperatures, using silver-alumina based catalysts and realistic exhaust-gas conditions and addition of hydrogen, as produced in a reformer system.

A high C/N ratio and addition of hydrogen has a positive influence on the NO_x conversion. However, as was seen for the 2%Ag sample, provided 1000 ppm of hydrogen is added to the feed, a relatively high NO_x conversion can be achieved at a low C/N ratio, albeit at high temperature (300 °C). Adding trace amounts of platinum (100 ppm by weight) to the 2%Ag catalyst significantly increases the NOx conversion at high C/N ratios. Further addition of hydrogen also enhances the activity over the Pt doped catalyst, compared to the 2%Ag sample, also at lower C/N ratios. The results for the samples with high silver loading show similar trends as for the Pt doped catalyst, with high NOx conversion at high C/N ratios. This implies that platinum may act as oxidation site, needed for the partial oxidation of the reducing agent.

NH_3 formation is promoted by a high C/N ratio and hydrogen feed, but is not necessarily coupled to a high NO_x conversion. A high NH_3 formation is observed only over the high loaded samples, while the low loaded samples consistently show a low NH_3 formation, regardless of NO_x conversion. Thus, it is concluded that the NH_3 formation is promoted by high silver loading. The formed ammonia may be used in a dual SCR system to increase the total NO_x reduction and to reduce the fuel penalty.

It is shown that the production of hydrogen corresponding to 1000 ppm hydrogen addition to the feed results in an unacceptable fuel penalty, compared to urea-SCR. It is concluded that the amount of hydrogen added to the LNR must be reduced in real applications.

Acknowledgements

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Table captions

Table 1: Washcoat properties for the powder support and catalyst (ATR) used in this study. For the powder catalyst, the subscripts in the molecular formula reveal the nominal weight loading of the active metals and promoters on the alumina support. The surface area and porosity were measured by N_2-BET while the crystallite size of ceria was measured by XRD using the Scherrer equation at Bragg angle 2θ=28.5°.

Table 2: Sample preparation methods, nominal silver loading and specific surface area for LNR catalyst samples.

Table 3: Binding energies and surface atomic ratios for the fresh powder sample $Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta$-$Al_2O_3$

Table 4: Results for ATR of standard diesel fuel over catalyst $Rh_{1.0}Pt_{1.0}Ce_{10}La_{5.0}/\delta$-$Al_2O_3$ at H_2O/C=3.0, O_2=0.49 (λ=0.33), GHSV~17700 h^{-1}.

Table 5: NH_3 formation without hydrogen addition, for C/N=3 and C/N=12 with *n*-octane as reductant at 200, 250 and 300 °C for 2%Ag, 2%AgPt100, 5%Ag and Mix samples. Inlet conditions: 200 ppm NO, 5% H_2O, 6% CO_2 and 10% O_2 (Ar bal.). CO concentrations are stated in the table. GHSV=33, 300 h^{-1}.

Table 6: Calculated total NO_x reduction for a theoretical dual SCR system. Gas feed over the HC-SCR catalyst: 200 ppm NO, 5% H_2O, 6% CO_2 and 10% O_2 (Ar bal.), with A: 350 ppm CO or B: 850 ppm CO or C: 350 ppm CO, 1000 ppm H_2 or D: 850 ppm CO, 1000 ppm H_2. C/N=12, with *n*-octane as reductant. GHSV=33, 300 h^{-1}.

Figure captions

Figure 1: NO_x conversion for C/N=3 (left) and C/N=12 (right) at 200, 250 and 300 °C with *n*-octane as reductant and 1000 ppm H_2 in the feed for 2%Ag (○), 2%AgPt100 (□), 5%Ag (+) and Mix (×) samples. Inlet conditions: 200 ppm NO, 1000 ppm H_2, 5% H_2O, 6% CO_2 and 10% O_2 (Ar bal.). CO concentrations are stated in the figure. GHSV=33, 300 h^{-1}.

Figure 2: NO_x conversion at 250 °C with *n*-octane as reductant and 3000 ppm H_2 in the feed for 2%Ag (○), 2%AgPt100 (□), 5%Ag (+) and Mix (×) samples. Inlet conditions: 200 ppm NO, 3000 ppm H_2, 5% H_2O, 6% CO_2 and 10% O_2 (Ar bal.). CO concentrations are stated in the figure. GHSV=33, 300 h^{-1}.

Figure 3: NH_3 formation for C/N=3 (left) and C/N=12 (right) at 200, 250 and 300 °C with *n*-octane as reductant and 1000 ppm H_2 in the feed for 2%Ag (○), 2%AgPt100 (□), 5%Ag (+) and Mix (×) samples. Inlet conditions: 200 ppm NO, 1000 ppm H_2, 5% H_2O, 6% CO_2 and 10% O_2 (Ar bal.). CO and H_2 concentrations are stated in the figure. GHSV=33, 300 h^{-1}.

Figure 4: NH_3 formation at 250 °C with *n*-octane as reductant and 3000 ppm H_2 in the feed for 2%Ag (○), 2%AgPt100 (□), 5%Ag (+) and Mix (×) samples. Inlet conditions: 200 ppm NO, 3000 ppm H_2, 5% H_2O, 6% CO_2 and 10% O_2 (Ar bal.). CO concentrations are stated in the figure. GHSV=33, 300 h^{-1}.

Figures

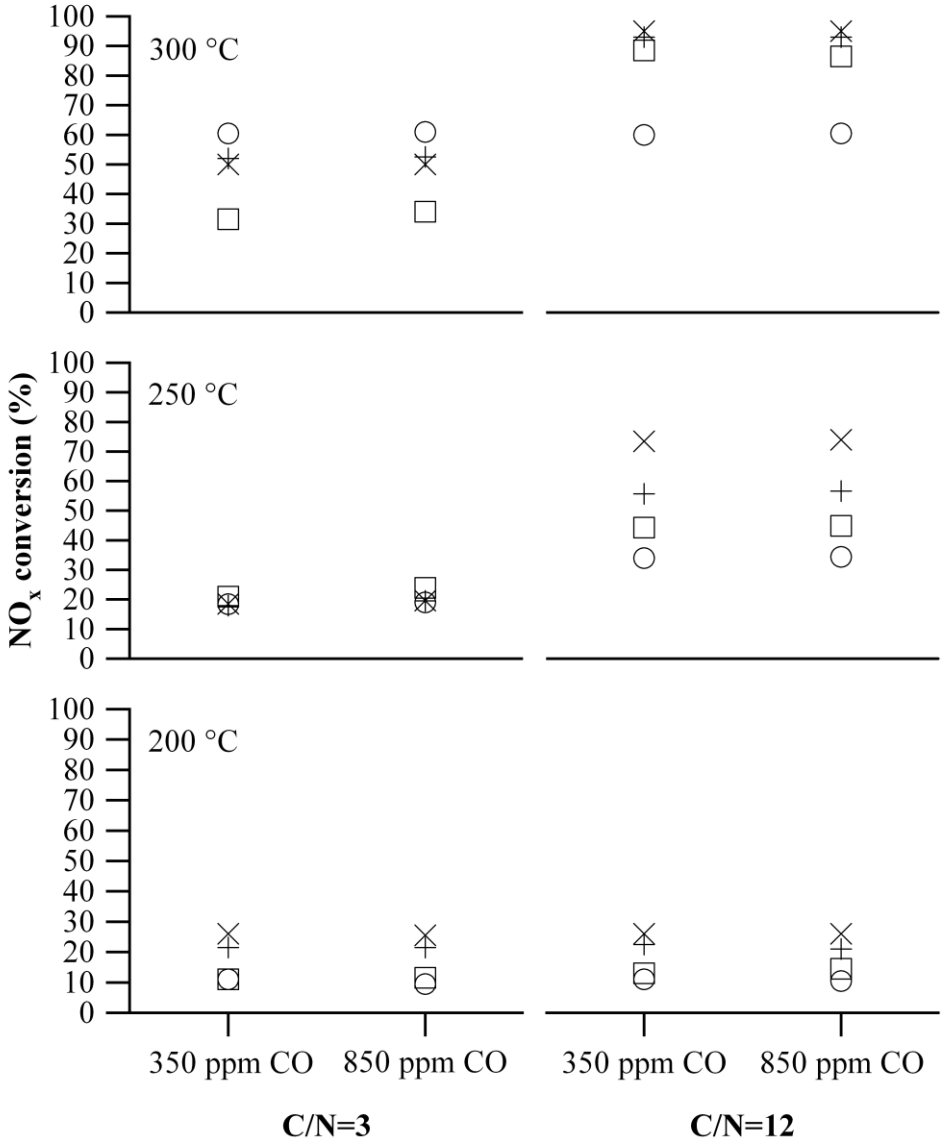

Figure 1

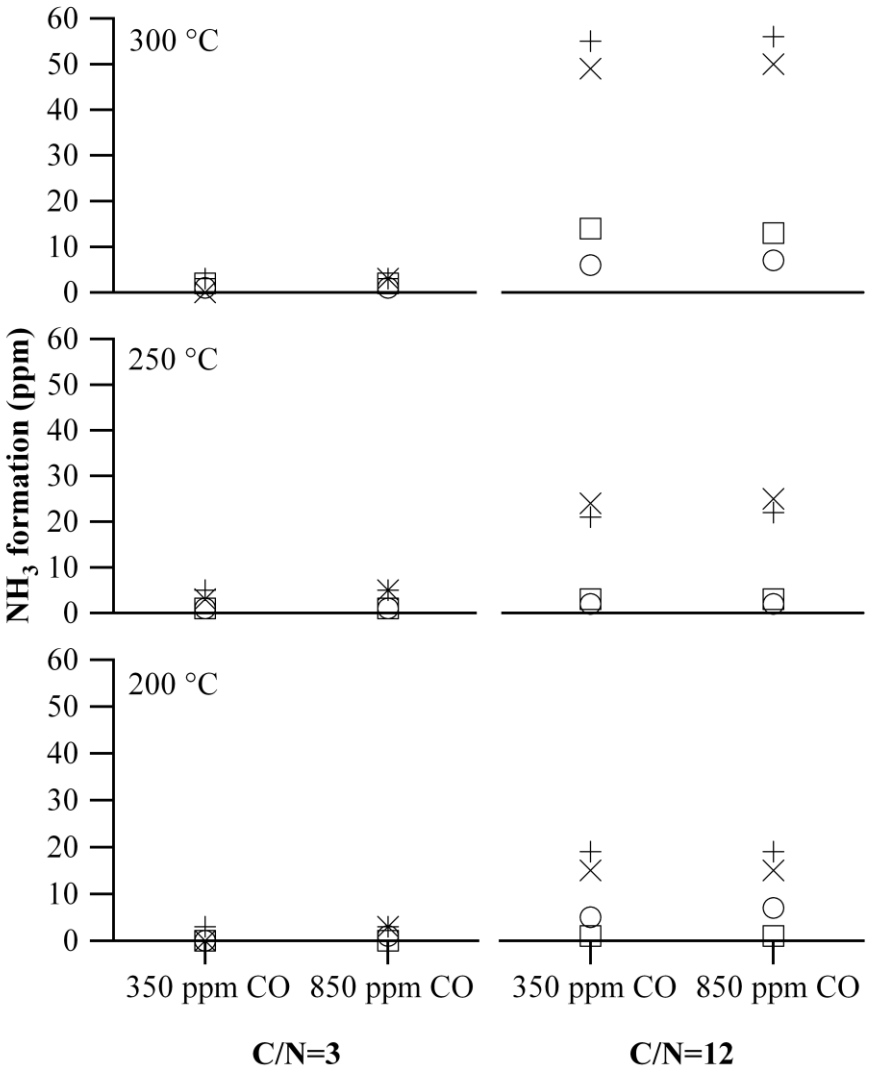
300 °C
250 °C
200 °C
NH3 formation (ppm)
60
50
40
30
20
10
0
350 ppm CO
850 ppm CO
350 ppm CO
850 ppm CO
C/N=3
C/N=12

Figure 2

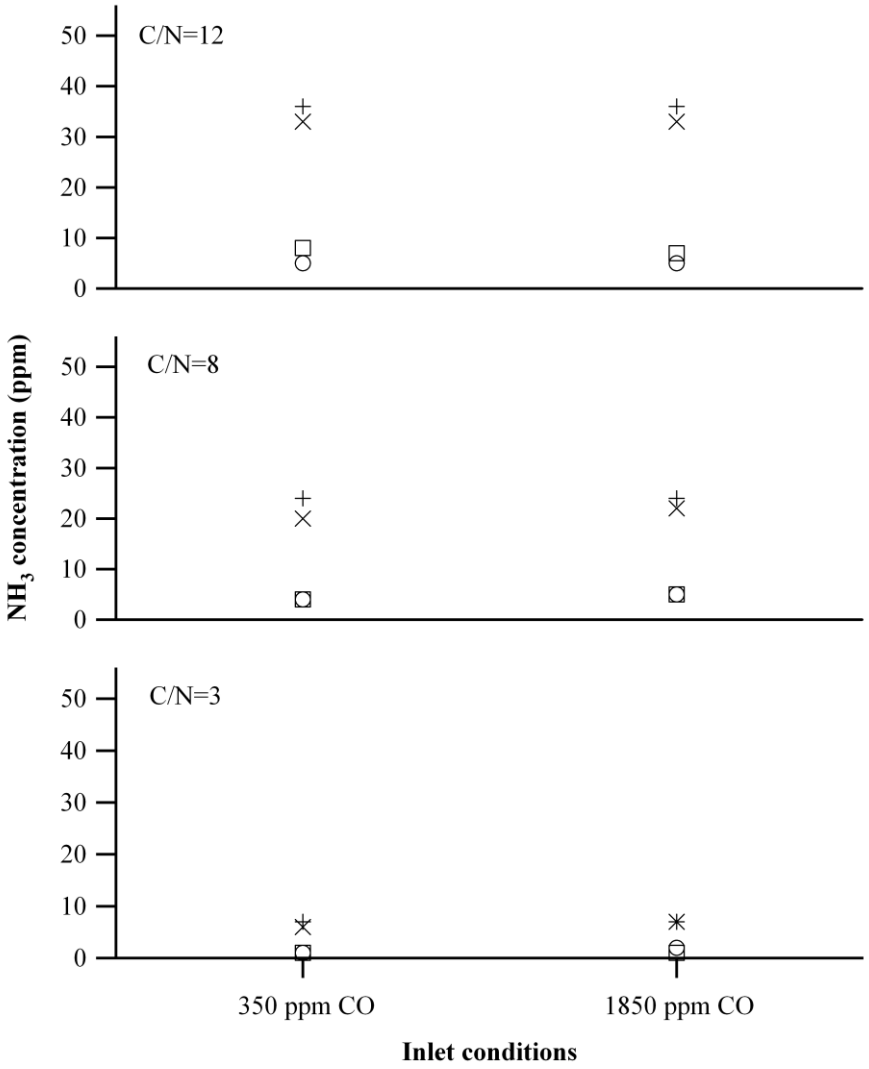
C/N=12
C/N=8
C/N=3
50
40
30
20
10
0
NH3 concentration (ppm)
350 ppm CO
1850 ppm CO
Inlet conditions

Figure 3

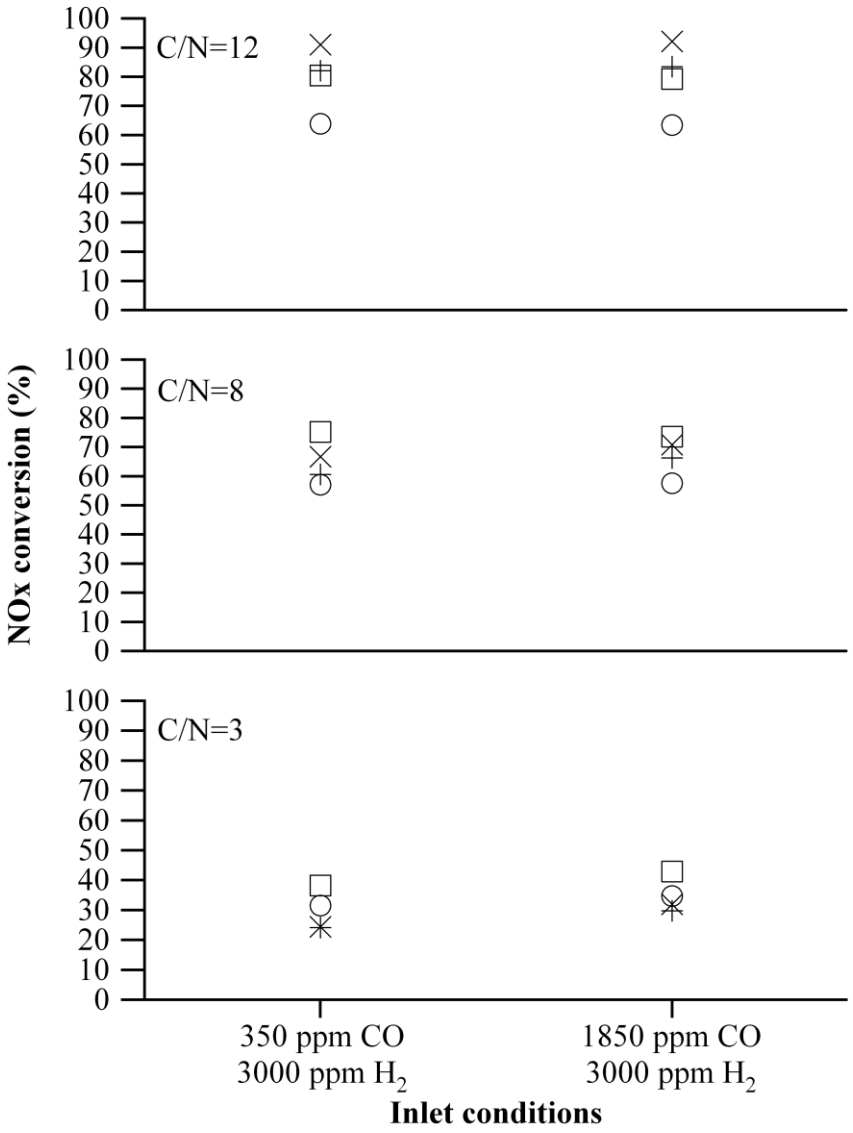
C/N=12
C/N=8
C/N=3
NOx conversion (%)
100
90
80
70
60
50
40
30
20
10
0
350 ppm CO
3000 ppm H2
1850 ppm CO
3000 ppm H2
Inlet conditions

Figure 4