Short communication

# Ammonia formation from nitric oxide over Pd-based catalysts in multicomponent feed gas compositions

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## ABSTRACT

Using multicomponent gas feeds, the formation of ammonia from nitric oxide over $Pd/Al_2O_3$ and $Pd/Ce/Al_2O_3$ model catalysts was compared to that of a commercially-available three-way catalyst. Steady-state oxygen-sweep experiments show that the highest activity for ammonia formation is obtained over the $Pd/Ce/Al_2O_3$ catalyst whilst the lowest activity is observed for the three-way catalyst. The latter is considered to be linked to the incorporation of rhodium, a component that promotes the $NO_x$ reduction selectivity towards $N_2$. Also, lean/rich cycling experiments were carried out to simulate the cycling conditions that passive-SCR after treatment systems depend upon. High activity is again seen over the $Pd/Ce/Al_2O_3$ catalyst during short periodic switches. For the three-way catalyst, longer periodic switches are required for the onset of ammonia formation due to the high oxygen storage capacity of this sample as compared to the other two. Hence, a future direction of investigation could be to develop materials with equivalent water-gas shift properties of ceria, but with reduced oxygen storage capacity so as to provide hydrogen for reaction without incurring a significant delay in ammonia formation.

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## 1. Introduction

The fuel economy of gasoline fuelled vehicles can be improved by ensuring that the combustion takes place in the presence of excess oxygen, so-called lean operation [1]. Lean operation however, makes it challenging to reduce nitrogen oxides ($NO_x$) to $N_2$, driving the development for new $NO_x$ abatement concepts whereby the fuel economy can be improved whilst the tailpipe emissions are kept sufficiently low to fulfill future, and increasingly stringent, regulations [2–4].

Passive-SCR is a newly emerging technique for $NO_x$ abatement in both diesel and lean-burn spark ignition gasoline passenger vehicles. The concept of this technique is to generate an onboard supply of $NH_3$ in the vehicle by utilizing the $NO_x$ that is readily available in the exhaust stream. The formed $NH_3$ can then be stored in an SCR catalyst placed downstream of the ammonia formation catalyst and used to reduce slipped $NO_x$ when the engine operates under lean conditions. If sufficient amounts of $NH_3$ can be produced during rich operation (low air-to-fuel ratio) and stored for complete reaction

with $NO_x$ to form $N_2$ during the subsequent lean periods, an external urea injection system, as required by current $NH_3$-SCR technology, may not be needed [5–7].

We have previously identified $Pd/Ce/Al_2O_3$ as a promising catalyst formulation for ammonia formation in model gas compositions, i.e. NO + $H_2$ or NO + CO + $H_2O$ [8]. However, in order to identify this formulation as appropriate for real-life applications, it is also important to investigate the activity for $NH_3$ formation in more complex feed compositions relevant to those one would encounter onboard a lean-burn gasoline vehicle. DiGuillio et al. have recently examined ammonia formation over a series of three-way catalysts (TWCs) for passive-SCR systems using gas mixtures containing NO, CO, $H_2$, $C_3H_6$, $CO_2$ and $H_2O$ [5]. In their systematic study, the authors identify through means of both steady-state and cycling experiments that the formation of $NH_3$ is highly dependent on several factors, including the air-to-fuel ratio, temperature and catalyst formulation. The objective of the present study is to add to the basic understanding of how components commonly included in three-way catalysts promote/inhibit ammonia formation when multicomponent feed gas compositions are used. This is approached by systematically comparing ammonia formation as a function of feed gas stoichiometry, as used by DiGuillio et al. [5], for model catalysts with reduced complexity, i.e. $Pd/Al_2O_3$ and $Pd/Ce/Al_2O_3$, and a commercially available TWC.

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## 2. Experimental

### 2.1. Materials

Three washcoated cordierite monolith substrates were investigated; (i) a commercially available three-way catalyst (TWC) containing Pd (28 g/ft$^3$) and Rh (3 g/ft$^3$) in addition to other materials such as cerium, zirconium and barium, (ii) a model Pd/Al$_2$O$_3$ catalyst (21 g/ft$^3$) and (iii) a model Pd/Ce/Al$_2$O$_3$ catalyst (12 g/ft$^3$), prepared in-house via incipient wetness impregnation (method described in detail elsewhere [8]).

### 2.2. Catalytic evaluation

Catalytic activity measurements were conducted using a continuous flow reactor as described by Kannisto et al. [9]. In short, the system consists of a quartz tube surrounded with a heating coil and insulation. It contains two thermocouples to measure the temperature 10 mm before and in the centre of the monolith sample. Two uncoated (blank) cordierite monoliths were placed on either side of the sample monolith in the quartz tube to minimize temperature gradients in the sample by reducing axial radiation heat losses. With this arrangement, a nearly isothermal sample (temperature gradients below 1 ° C) is achieved when cooling/heating in Argon only [10]. The inlet gas composition was controlled using mass flow controllers (Bronkhorst Hi-Tech LOW-ΔP-FLOW) and the outlet gas composition was analyzed using an FTIR gas-analyzer (MKS 2030 HS) with a gas sampling cell volume of 200 ml. With the total flow used here the response time for a step-change between two stationary levels is 20–23 s [11]. All experiments were carried out with an Ar balance in order to keep the total gas flow constant at 1000 ml/min, corresponding to a gas hourly space velocity (GHSV) of 20,000 h$^{-1}$. Prior to the activity measurements, the monolith samples were exposed to 2 vol % O$_2$ at 500 ° C for 30 min in order to remove pre-adsorbed carbonaceous species from the surface.

#### 2.2.1. Steady-state experiments

Steady-state experiments were conducted in order to measure the formation of NH$_3$ that could be achieved over each sample as a function of the stoichiometric-value (S-value) of the feed. The S-value characterizes the net oxidizing-reducing character of the inlet feed gas composition and is calculated according to the following equation [12]:

$$S = \frac{2[O_2] + [NO]}{[CO] + [H_2] + 9[C_3H_6]}. \tag{1}$$

Calculated S-values less than 1 represent gas compositions which are net-reducing in character. When S is equal to 1, the fed stream is at the stoichiometric point, whilst feeds resulting in S-values above 1 are net-oxidizing. Feed gas compositions with constant concentrations of NO, CO, H$_2$, C$_3$H$_6$, CO$_2$ and H$_2$ were fed whilst the concentration of O$_2$ available at each S-value was changed, as shown in Table 1. All experimental protocols were carried out at an inlet temperature of 500 ° C.

#### 2.2.2. Cycling experiments

As passive-SCR is a technology that depends on dynamic switching between rich and lean engine operation, it is of vital importance to determine how the catalysts perform under transient conditions. The feed gas composition was therefore altered between a large excess of oxygen (8 vol %) and S = 0.688 for eight cycles in order for a reproducible response to be achieved for each sample. The S-value of the lean conditions could not be calculated according to Eq. (1) due to the absence of reducing species in the feed. Two cycling periods (long and short) were investigated. During the long periods, the feed was kept at S = 0.688 for 60 s, before switching to the feed containing 8 vol % O$_2$ for 120 s. For the short periods, the corresponding time was 20 and 40 s respectively.

#### 2.2.3. Oxygen storage experiments

The dynamic oxygen storage capacity (OSC) at 500 ° C of each sample was determined using a reactor setup similar to that described above. However, the total flow used was 300 ml/min and solenoid valves were used to allow rapid exchange of gases. A more detailed description of the reactor setup has been reported elsewhere [13]. The samples were pretreated at 500 ° C in a flow of O$_2$ in order to remove any pre-adsorbed carbonaceous species and subsequently reduced by flowing CO. The sample was then exposed to alternate 30 second pulses of either 2 vol % O$_2$ or 4 vol % CO, with a 60 second interval containing Ar only between each pulse in order for weakly-bound oxygen to desorb from the catalyst surface. This cycle was repeated seven times so that reproducible responses were obtained. The dynamic OSC was then quantified in terms of micromoles of CO$_2$ produced per sample (washcoat + cordierite substrate).

## 3. Results and discussion

Fig. 1 shows the steady-state formation of ammonia at 500 ° C over the samples as a function of the S-value of the feed gas composition. For all samples, the highest amount of NH$_3$ is formed at the lowest S-value, 0.529. The NH$_3$ formation then decreases as the feed becomes increasingly oxidizing. For the highest S-value investigated, S = 1.009, no formation of NH$_3$ is detected for any of the investigated samples. When S<1, the highest concentrations of NH$_3$ are formed over the Pd/Ce/Al$_2$O$_3$ sample, whilst the lowest concentrations are formed over the TWC. The formation of NH$_3$ from NO and H$_2$ over noble metals has been well documented since the early development of the TWC in the 1970s [14–16]. The reaction involves dissociative adsorption of NO on noble metal sites, platinum and palladium based catalysts are reported as having exceptionally high activity [14]. The higher activity for NH$_3$ formation over Pd compared to Pt with regards to temperature range and presence of CO has also been recognised [4]. In the presence of CO, surface-bound isocyanate groups can be formed from CO and dissociated NO before being hydrolysed to form ammonia [17,18]. Although palladium has been

**Table 1**
Feed gas compositions during steady-state and cycling measurements. The stoichiometric number (S) is defined as $(2[O_2] + [NO])/([CO] + [H_2] + 9[C_3H_6])$.

| Stoichiometric number (S) | O$_2$ (%) | NO (%) | CO (%) | H$_2$ (%) | C$_3$H$_6$ (%) | CO$_2$ (%) | H$_2$O (%) |
|---|---|---|---|---|---|---|---|
| – | 8.00 | 0.075 | – | – | – | 5.0 | 5.0 |
| 1.009 | 1.590 | 0.15 | 1.8 | 0.60 | 0.10 | 5.0 | 5.0 |
| 0.970 | 1.525 | 0.15 | 1.8 | 0.60 | 0.10 | 5.0 | 5.0 |
| 0.961 | 1.510 | 0.15 | 1.8 | 0.60 | 0.10 | 5.0 | 5.0 |
| 0.858 | 1.340 | 0.15 | 1.8 | 0.60 | 0.10 | 5.0 | 5.0 |
| 0.688 | 1.060 | 0.15 | 1.8 | 0.60 | 0.10 | 5.0 | 5.0 |
| 0.529 | 0.790 | 0.15 | 1.8 | 0.60 | 0.10 | 5.0 | 5.0 |