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Ammonia formation over Pd/Al_2O_3 modified with cerium and barium

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Abstract

We report experimental results for ammonia formation from nitric oxide and either a direct source of hydrogen or from a mixture of carbon monoxide and water over palladium based catalysts. Specifically, the addition of barium or cerium into an alumina supported palladium sample was studied. Static and transient flow reactor experiments were performed in order to identify the effects of temperature and the presence of oxygen on the activity for ammonia formation. Modification of Pd/Al_2O_3 with cerium proved to be beneficial for the activity due mainly to its enhancement of the water-gas-shift reaction, thus providing a higher availability of hydrogen for ammonia formation, but also because it remains active in the presence of slightly oxidizing global conditions when hydrogen is provided directly to the feed. Although the modification of Pd/Al_2O_3 with barium did not affect the ammonia formation during static conditions, the activity during lean/rich cycling increased. This is important for applications of passive selective catalytic reduction.

Keywords: Catalytic exhaust aftertreatment, Passive-SCR, NO_x reduction, NH_3 formation,

1. Introduction

Combustion of gasoline and diesel in vehicles results in the formation of harmful products, including nitrogen oxides (NO_x), which are known to be responsible for various environmental issues such as photochemical smog and acid rain [1, 2]. At present, 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 [3]. Practically, lean operation makes it challenging to reduce NO_x to N_2, driving the development for new NO_x abatement concepts such as NO_x storage reduction (NSR) and selective catalytic reduction (SCR) whereby the fuel economy can be improved whilst the tailpipe emissions are kept sufficiently low to fulfill future, and increasingly stringent, regulations [4, 5, 6, 7]. Selective catalytic reduction of NO_x with ammonia (NH_3-SCR) is currently the preferred technology for NO_x abatement from stationary sources and larger vehicles including trucks and buses [8]. This technique relies on selective reduction of NO_x with NH_3 over a suitable catalyst to form N_2 in the presence of elevated levels of O_2 [2, 9]. However, due to concerns with the safety and toxicity associated with ammonia transportation and storage, the NH_3 is stored in the form of urea-in-water solution on-board the vehicle. Although this technique is acceptable for heavy-duty vehicles, difficulties arise when applied to smaller passenger cars. Some of the problems encountered are due to extra weight associated with the need for an additional urea storage tank as well as the urea injection system, which is complex, costly and increases the risk of creating an NH_3 slip [2, 5, 10]. Ammonia emissions are undesirable since NH_3 is a toxic air pollutant and is known to contribute to the production of secondary particulate matter [11, 12].

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. Although the current concept of this technique is to produce NH_3 whilst the engine undergoes rich operation (low air-to-fuel ratio), a long-term goal is to suggest methods and/or catalyst formulations which would allow the formation of NH_3 under stoichometric or even slightly lean conditions, thereby minimizing the fuel penalty incurred during the periods required for NH_3 formation. 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 is set back to operate under lean conditions. If sufficient amounts of NH_3 can be produced during the rich periods 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

2

be needed [13, 14, 15].

Another technique, which also depends on periodic cycling between lean and rich operation, is the afore-mentioned NSR system. A well-studied material used for this application is $Pt/Ba/Al_2O_3$, over which NH_3 formation has previously been observed during operational switches. Castoldi et al. [16] report that, as the Ba content of the formulation is increased, the amount of NH_3 formed over the catalyst by the reaction of stored NO_x with H_2 also increases but is only observed after the formation of N_2 has diminished. As reported by Pihl et al. [17] and Cumaranatunge et al. [18] this may be related to the fact that NH_3 can be generated in significant quantities at the catalyst inlet but as it progresses axially through the catalyst it acts as a hydrogen carrier, reducing stored NO_x to N_2. This was confirmed by Clayton et al. [19] who also determined that the reactivity of NH_3 and H_2 with stored NO_x is comparable at temperatures above 230 °C.

In automotive applications however, deviations in driving patterns result in conditions where the concentration of H_2 present in the exhaust stream does not meet the requirement for ammonia formation for significant periods. Despite this, passive SCR may play an important role in NO_x abatement provided that a direct supply of H_2 is not necessary. Carbon monoxide and water are also present in the exhausts during rich operation [20] and H_2 can be formed by the water-gas-shift (WGS) reaction;

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{1}$$
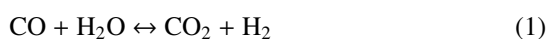
Hence, water could be a viable hydrogen source for the further formation of NH_3. Ceria, particularly when metal-modified, has been extensively studied due to its excellent properties that catalyze the WGS reaction. When metal-modified, the oxygen storage capacity (OSC) and reducibility of the ceria support increase [21, 22]. The reducibility of the ceria support is of importance since it is able to utilise lattice oxygen to facilitate the exchange process $2CeO_2 \leftrightarrow Ce_2O_3 + 1/2O_2$, thereby resulting in an oxygen vacancy. Thus for the water-gas-shift reaction, CO is able to adsorb onto metal sites whilst H_2O dissociation takes place on the oxide vacancy, resulting in

high activity [22].

As we reported previously, Pd/Al_2O_3 is a promising material for passive SCR, over which high selectivity to NH_3 can be achieved over a broad temperature interval [23]. The objective of the present study is to to investigate whether the modification of Pd/Al_2O_3 with cerium or barium can further enhance the temperature interval for NH_3 formation from $NO + H_2$ and $NO + H_2O +$ CO feed gas compositions. Since passive SCR is a technique that depends on periodic switching between rich and lean operating conditions, the influence of the presence of O_2 on the ammonia formation is also of interest and is studied by use of both steady-state (oxygen-step) and transient (oxygen-pulse) experiments.

2. Experimental section

2.1. Catalyst preparation and characterisation

A 30 g batch of 0.5 wt.% Pd/Al_2O_3 was prepared via incipient wetness impregnation of an aqueous Pd precursor solution $((NH_3)_4Pd(NO_3)_2)$ into a commercially-available γ-Al_2O_3 support material (Puralox SBa200). The prepared sample was subsequently frozen in liquid N_2 and freeze-dried for approximately 12 h to ensure complete sublimation of water with preserved dispersion of Pd and minimal damage to the support structure. The obtained powder catalyst was then calcined in air at 550 °C for 1 h.

The prepared Pd/Al_2O_3 catalyst was then divided into three aliquots, two of which underwent subsequent modification with either cerium or barium. The same Pd/Al_2O_3 sample was used for further impregnation in order to keep the noble-metal particle distribution and size constant in all samples being investigated. Barium and cerium containing samples were prepared to a nominal loading of 10 wt.% (calculation based on pure Ba and Ce) using aqueous solutions of $Ba(NO_3)_2$ and $Ce(NO_3)_2$ respectively. In order to stabilize Ba in the form of $BaCO_3$, a successive impregnation step was carried out on this sample using an aqueous solution of ammonium carbamate [24]. All samples were then freeze-dried and calcined in air at 550 °C for 1 h after each impregnation step.

The powder catalysts were then coated onto cordierite monolith substrates. This was done by

preparing solutions consisting of the powder catalyst, a suitable binder material (Disperal P2), water and ethanol. The monolith was then carefully immersed into the slurry, allowing the catalyst-containing liquid to be dispersed evenly throughout the channels by capillary forces. The monolith was then dried in air at 90 °C for two minutes to remove the water and ethanol, before being briefly calcined in air for a further two minutes at 500 °C and weighed. If necessary, the process was repeated until the desired mass of catalyst and binder was deposited (200 ± 3 mg). Once coated, the monoliths were calcined in air at 600 °C for two hours to ensure complete removal of water and phase transformation of the Disperal P2 to alumina.

The specific surface area of the prepared powder samples was measured by nitrogen physisorption at -196 °C using an ASAP 2010 (Micrometrics) sorptometer. Prior to adsorption, all samples were dried at 200 °C for two hours under vacuum in order to remove any residual water. Respective surface areas were then determined according to the standard Brunauer-Emmet-Teller (BET) method [25] using $P/P_0 = 0.05 - 0.20$. The specific surface area of the pure support materials; both fresh and after calcination in air at 600 °C for one hour, was measured to determine the thermal stability of the supports. The prepared powder catalysts were characterised directly after calcination.

The distribution of Pd, Ba and Ce particles throughout the alumina carrier phase was determined by scanning transmission electron microscopy coupled with energy-dispersive X-ray spectroscopy (STEM-EDX). This allowed the confirmation of a successful synthesis procedure. A small amount of the prepared sample was crushed together with ethanol to form a suspension which was subsequently ultrasonicated for one minute. One drop of the suspension was then applied to a Cu-grid coated with continuous carbon. STEM-EDX maps were then acquired at a spot size of 5, corresponding to a beam current of 0.7 nA, using an FEI-Talos electron microscope. Aperture sizes of 2,000 and 70 μm were selected with a camera length of 125 cm. The minimum time for elemental mapping of the sample was 10 minutes.

2.2. Kinetic measurements in gas flow reactor

Continuous gas flow reactor studies were carried out to determine the activity and selectivity of the prepared catalysts. The reactor setup employed in this investigation has previously been

described by Kannisto *et al.* [26]. 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 in order to reduce otherwise significant heat losses and achieve a nearly isothermal sample. The inlet gas composition was controlled using mass flow controllers (Bronkhorst Hi-Tech LOW-ΔP-FLOW) and the outlet gas composition was analysed using an FTIR gas-analyzer (MKS 2030 HS). All experiments were carried out with an Ar balance in order to keep the total gas flow constant at 2000 ml/min, corresponding to a gas hourly space velocity (GHSV) of 40,000 h^{-1}. Prior to kinetic analysis, all samples were pretreated in a flow of 5 vol % O_2 for 30 minutes at 500 °C in order to remove any carbonaceous contaminants from the monolith surface and allow fair comparison.

To investigate the temperature region for which the catalyst is active for ammonia formation, temperature programmed reaction experiments were conducted. All samples were exposed to feed compositions containing 500 ppm NO and either 1,500 ppm H_2 (feed gas A) or 1,500 ppm CO accompanied by 2 % H_2O (feed gas B). During exposure to both gas mixtures, the inlet temperature was varied from 500 to 120 °C at a rate of 7 °C/min. The system was then kept at this temperature for ten minutes before increasing the temperature to 500 °C at the same rate. The low ramp rate was chosen as to ensure nearly stationary conditions.

To evaluate the influence of the stoichiometric number, S, of the feed on the formation of NH_3 over the catalysts, steady-state experiments at 250, 350 and 450 °C were subsequently carried out. The S-value characterizes the net oxidizing-reducing character of the inlet feed and is defined as [27];

$$S = \frac{2[O_2]+[NO]}{[CO]+[H_2]} \qquad (2)$$

Again, the two feed compositions were fed to the reactor though this time various levels of oxygen were also added. The O_2 concentration was varied from 0.105 to 0.015 % (corresponding to S-values between 1.73 and 0.33) in steps of 150 ppm, each of which lasted for 20 minutes in

Table 1: Surface area characterisation of prepared samples.

	Surface Area (m^2/g)	Nominal composition (%)		
		Pd	Ba	Ce
Pd/Al$_2$O$_3$	185	0.5	-	-
Ba/Pd/Al$_2$O$_3$	160	0.5	10	-
Ce/Pd/Al$_2$O$_3$	152	0.5	-	10

order to allow steady state to be reached.

To determine the transient effect of switching between oxygen excess and deficient conditions, feed gas A or B was fed constantly to the reactor. A supply of 2 vol.% O_2 was then pulsed into the flow at periodic intervals of 4 minutes whereafter the O_2 pulse was extinguished to emulate rich conditions. A total of 10 lean/rich pulses were introduced in succession in order for a consistent, repeatable behaviour of the catalytic material to be obtained. It was typically seen that the initial 3-4 pulses in the sequence gave responses which were higher in concentration with time. After this, the concentration of NH_3 formed during each pulse was constant and reproducible.

3. Results

3.1. Catalyst characterization

The determined specific surface areas of the synthesized catalysts are displayed in Table 1. Here it can be seen that there is a small decrease in the specific surface area after further impregnation of the Pd/Al$_2$O$_3$ reference sample, with the Ce-modified sample exhibiting the lowest value.

The results from the STEM-EDX analysis of the Pd/Al$_2$O$_3$, Ce/Pd/Al$_2$O$_3$ and Ba/Pd/Al$_2$O$_3$ samples are displayed in Figures 1 - 3 respectively. As can be seen in Figure 1, the synthesis of Pd/Al$_2$O$_3$ resulted in a highly dispersed noble metal-phase throughout the support material. The Pd content throughout the sample was determined as 0.58 ± 0.26 wt.%. The variation in metal content calculated during the imaging conducted at different positions is explained by variations in the distribution of Pd on the microscopic scale. Barium was also found to be homogeneously distributed into the parent Pd/Al$_2$O$_3$ sample, which can be seen in Figure 2. In the top panels,
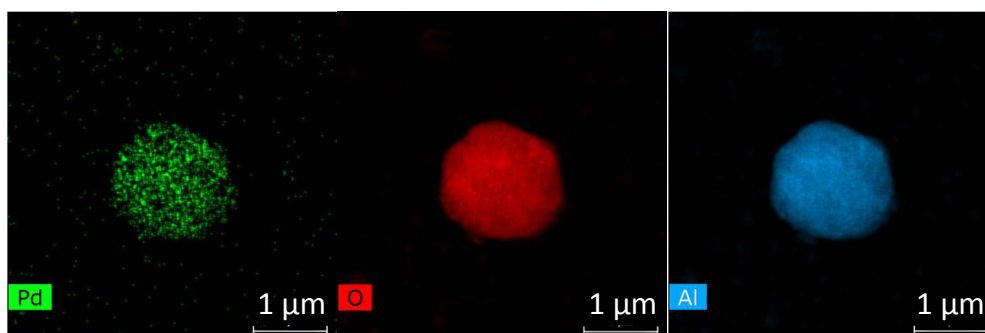
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Figure 1: STEM-EDX maps for Pd, O and Al for the 0.5 wt.% Pd/Al$_2$O$_3$ reference sample.

the presence of small, well-distributed regimes with barium, most likely in the form of baria, that are evenly distributed throughout the Al$_2$O$_3$ support is observed. The lower panels however, show that there are also larger needle-shaped regions of barium and oxygen likely in the form of Ba(OH)$_2$·H$_2$O, BaO crystallites present in the sample that are entirely separate from the alumina carrier phase. Figure 3 shows an obtained STEM-EDX image of the prepared Ce/Pd/Al$_2$O$_3$ sample. It can be observed that cerium is very well distributed throughout the Al$_2$O$_3$ support material with a particle size of approximately 5 - 10 nm in diameter.

3.2. Kinetic evaluation

Figure 4 shows the formation of NH$_3$ in the presence of NO and either a direct source of H$_2$ (panel a) or a combination of CO and H$_2$O (panel b) as a function of the inlet gas temperature. The inlet concentration of NO was 500 ppm and the chosen limiting reagent for this reaction, thus 500 ppm is the maximum concentration of NH$_3$ that can be generated under steady-state conditions. It can therefore be seen that complete conversion of NO to NH$_3$ is achieved over Pd/Al$_2$O$_3$ over the broad temperature range of 250 to 500 °C when H$_2$ is available for direct reaction in the feed, with the Ce-modified sample showing a similar (although slightly lower) conversion trend. Negligible amounts of N$_2$O were detected throughout the course of this reaction. Upon comparison of the WGS-assisted reaction, the temperature window for ammonia formation becomes more narrow where the Ce-modified sample is the most active sample with a light-off temperature for ammonia formation of approximately 220, compared to 250 °C as seen
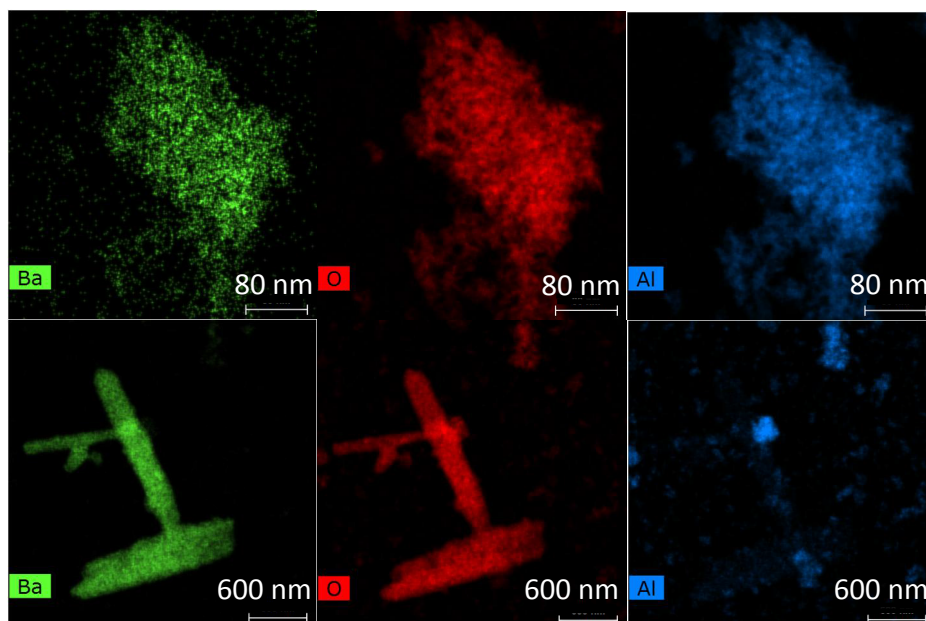
Figure 2: STEM-EDX maps for Ba, O and Al for 10 wt.% Ba/Pd/Al$_2$O$_3$.
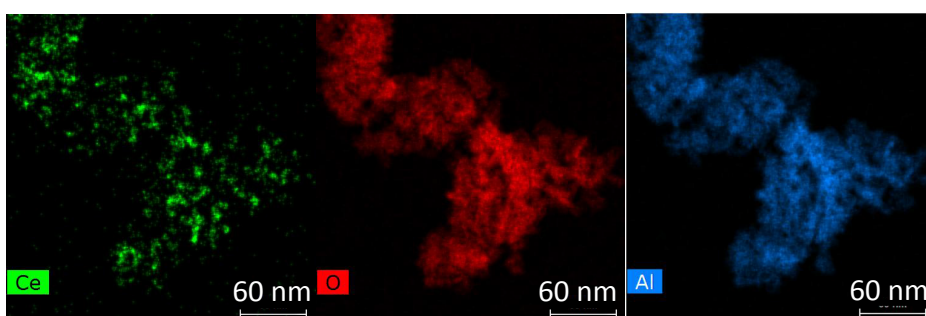

Figure 3: STEM-EDX maps for Ce, O and Al for 10 wt.% Ce/Pd/Al$_2$O$_3$.

for the non-modified and Ba-containing sample. The Ba-modified sample shows a maximum of around 50 % conversion of NO to NH$_3$ when exposed to both feed compositions although the temperature of this maximum shifts from 250 to 350 °C upon switching to H$_2$O as the source of hydrogen for NH$_3$ formation. Unlike the reaction when H$_2$ was directly available, N$_2$O is now detected in significant quantities over all samples. A maximum of ∼ 50 ppm is formed over the Pd/Al$_2$O$_3$ sample, centred at a temperature of approximately 270 °C. The addition of Ce and Ba to this formulation significantly enhances the amount of N$_2$O formed but shifts the formation
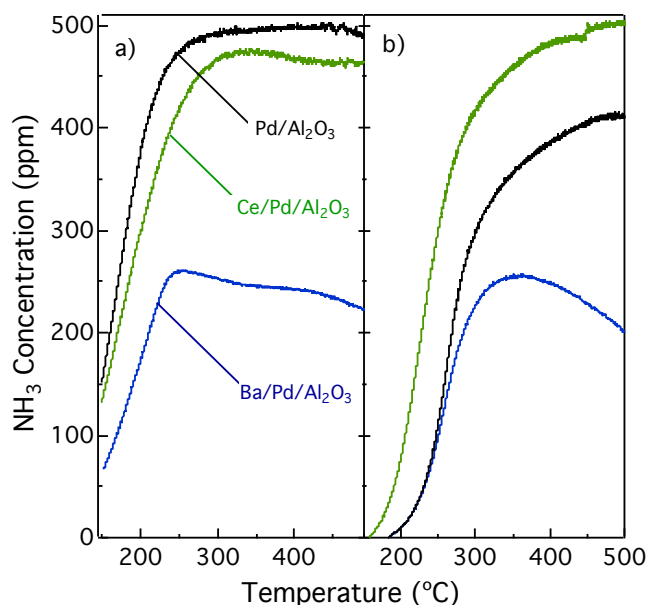
Figure 4: Ammonia formation over reference, Ce-modified and Ba-modified 0.5 wt.% Pd/Al_2O_3 during temperature programmed reaction in the presence of a) 500 ppm NO and 1,500 ppm H_2 (feed gas A) and b) 500 ppm NO, 1,500 ppm CO and 2 vol.% H_2O (feed gas B). Balance Ar is employed to maintain the space velocity at 40,000 h^{-1} and a temperature ramp rate of 7 °C/min was used.

towards lower temperatures, i.e. $\sim$ 100 ppm N_2O is formed over the Ba-modified sample at 220 °C and $\sim$ 140 ppm is formed over the Ce-modified sample at 200 °C.

Figure 5 shows the steady state formation of NH_3 from feed gas A (left-hand column) and B (right-hand column) over Pd/Al_2O_3 (a and d), $Ba/Pd/Al_2O_3$ (b and e) and $Ce/Pd/Al_2O_3$ (c and f) as a function of the stoichiometric number of the feed gas at 450, 350 and 250 °C. The dashed red line indicates the point where S = 1, indicating a stoichiometrically balanced feed. To the right of this line (S>1) the feed becomes net-oxidizing, whereas the left-hand side (S<1) represents net-reducing feeds. Higher amounts of NH_3 are formed over all catalysts when H_2 is directly available for reaction, i.e. no prerequisite reaction is required, as was seen by the temperature-programmed experiments previously discussed. For the majority of the experiments, the formation of NH_3 decreases as the stoichiometric number of the gas feed increases and is entirely suppressed when the feed becomes net-oxidizing. However, upon observation of the NH_3 formation over $Ce/Pd/Al_2O_3$ in the presence of NO and H_2, it can be seen that at low temperature
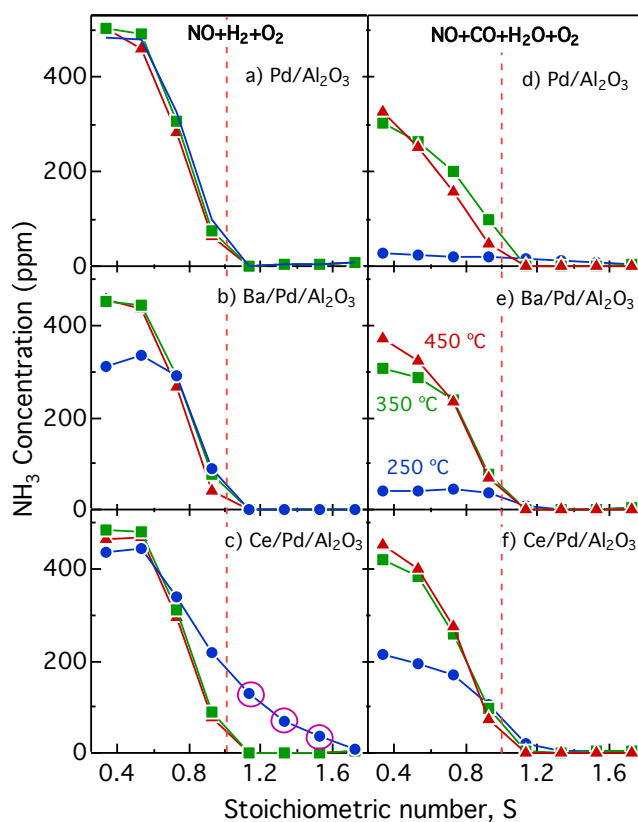
10

Figure 5: Steady-state formation of NH_3 as a function of the stoichiometric number, S, of the feed gas at 250, 350 and 450 °C over Pd/Al_2O_3 (a and d), $Ba/Pd/Al_2O_3$ (b and e) and $Ce/Pd/Al_2O_3$ (c and f) in the presence of 500 ppm NO with either 1,500 ppm H_2 (left-hand columns) or 1,500 ppm CO accompanied by 2 vol.% H_2O (right-hand columns). The O_2 concentration was varied between 0 and 1,050 ppm (S = 0.33 - 1.73) in steps of 150 ppm and Ar was used as balance to maintain GHSV = 40,000 h^{-1}. Highlighted data points represent responses which have not yet reached steady-state.

(250 °C) it is possible to produce low amounts of NH_3 even when S>1. A further trend regarding the Ce-modified sample is the increased activity for NH_3 formation in the presence of WGS reaction conditions compared to the other samples. In particular the low-temperature activity of this reaction is significantly enhanced, from almost no production of NH_3 over the reference Pd/Al_2O_3 sample to concentrations in slight excess of 200 ppm for the sample modified with Ce. Interestingly, the activity for NH_3 formation over the Ba-modified sample is higher during the experiments conducted in the presence of low concentrations of oxygen compared to the prior temperature programmed experiment performed in the absence of O_2. This observation is particularly noteable in the case where H_2 is directly available in the feed gas.

Figure 6 shows the transient behaviour of each sample when switching from rich to lean conditions for different temperatures in the presence of either feed gas A (left-hand column) or B (right-hand column). Formation of ammonia is observed for all samples immediately after O_2 is removed from the feed. In the presence of large excess of oxygen, however, no formation of NH_3 is observed over any sample. The barium-modified sample shows enhanced activity for NH_3 formation under transient conditions as compared to stationary conditions. This can be said of all temperature and gas feed compositions with the exception of the WGS-assisted reaction conducted at 250 °C (Figure 6f). Again, the benefit of impregnation of cerium into the catalyst formulation during WGS-assisted conditions can be seen and is especially pronounced during the rich phase of the transient experiment conducted at 250 °C where the ammonia formation is approximately 200 ppm higher over the $Ce/Pd/Al_2O_3$ sample compared to Pd/Al_2O_3 and $Ba/Pd/Al_2O_3$. With regards to N_2O formation during the low-temperature (250 °C) transient experiments, small amounts were observed during only the lean pulses when H_2 was available directly in the feed. Formation of approximately 20 ppm N_2O was observed over all catalyst formulations. Conversely, in the WGS-assisted experiments, N_2O was only detected during the rich phases. Furthermore, the formation of N_2O over the Ba- and Ce-modified samples was higher ($\sim$ 65 ppm) compared to the Pd/Al_2O_3 sample ($\sim$ 15 ppm).

4. Discussion

In line with the previous study [23], we have shown that alumina supported palladium catalysts are suitable for the selective reaction of NO to NH_3 using both a direct source of hydrogen but also hydrogen formed from H_2O and CO via the WGS reaction. However, in the present study an extra layer of complexity has been added by including a third component, i.e. barium or cerium, to the Pd/Al_2O_3 reference sample. To allow fair comparison of the investigated formulations, a first-stage synthesis of 0.5 wt.% Pd/Al_2O_3 was performed in order to serve as a reference catalyst. This reference material was subsequently split into three aliquots, two of which underwent subsequent modification by impregnation with aqueous solutions of either barium or cerium precursor salts. This method assumed that the dispersion of Pd throughout the parent
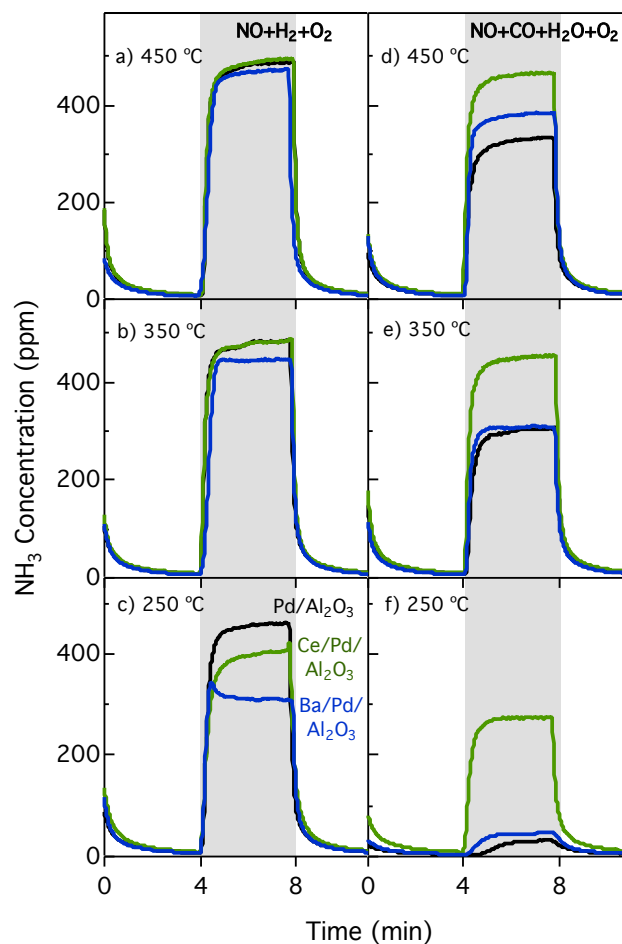
12

Figure 6: Transient formation of NH_3 over reference, Ce-modified and Ba-modified 0.5 wt.% Pd/Al_2O_3 formed during lean/rich cycling versus the time of reaction. Each reaction protocol was conducted in the presence of gas feed containing 500 ppm NO and either 1,500 ppm H_2 (left-hand column) or 1,500 ppm CO accompanied by 2 vol.% H_2O (right-hand column) at an inlet temperature of either 450 (a and d) 350 (b and e) or 250 °C (c and f). Ar balance was employed to maintain GHSV = 40,000 h^{-1}. Grey panels indicate the switch from lean to rich conditions by removal of oxygen from the feed gas.

sample was homogeneous so that the noble metal particle size distribution in each impregnated sample could be considered equal and therefore comparable, resulting in the additionally impregnated compound (i.e., Ce or Ba) being the only factor responsible for observed differences in activity. Márquez *et al.* [28] report on the modelling of the preferred adsorption sites of Pd atoms onto the surface of a stable (100) γ-alumina support. They state that strong (-3.81 to -

3.27 eV) and localized bonds are formed between Pd and tetrahedral sites of the alumina. As the synthesised Pd/Al_2O_3 catalyst was stabilised through calcination, it is highly unlikely that the active phase would undergo any significant change as a result of the secondary impregnation step conducted at room temperature. Thus, the Pd structure is considered to be similar in all as-prepared samples. However, due to strong metal-support interaction (SMSI) during reaction, ammonia formation may be suppressed. This will be discussed more below.

The formation of NH_3 from NO and H_2 was studied in the late 70s when the TWC was being developed for automotive applications. It has been reported that noble metal particles contain the active sites required for this reaction to take place efficiently [29, 30]. Thus it could be expected that, for the reaction of NO with H_2, the formation of NH_3 would be similar over all three samples if the number and properties of available active sites in the samples are the same. Although the NH_3 formation over the cerium-modified sample is similar though slightly lower compared to the reference sample when H_2 is directly available, the barium-modified sample forms significantly less NH_3. This is most obvious in the temperature programmed experiments in Figure 4a. This may indicate that the availability of palladium sites, active for NH_3 formation, has decreased as a result of the second impregnation step. It has been reported that when Pt/Al_2O_3 catalysts are impregnated with Ba, the Pt sites can become partially covered with BaO, decreasing the number of available Pt sites [16, 31]. Wang *et al.* have also reported on this effect and concluded it is due to the SMSI effect between barium and the noble metal [32]. Furthermore, the authors found that the coverage of Pt by barium is reversible, dependent on the environment the sample is exposed to. Under reducing conditions, barium migrates towards Pt and covers a portion of the Pt sites, whereas under oxidizing conditions barium migrates from the Pt sites. As the conditions of the temperature programmed experiments are strongly reducing, it is possible that partial encapsulation of Pd by both barium and cerium contribute to the loss in NH_3 formation. Effectively, this would lead to a lower conversion of NO due to lower number of available sites active for NO dissociation. Although this may explain the slightly lower NH_3 formation observed over the Ce-modified sample, such site blockage cannot be solely responsible for the significantly lower formation of NH_3 observed for the Ba-modified sample. Furthermore, storage of nitrogen

14

oxides is ruled out, not only because rich conditions are employed, but also because the length of experiment is sufficiently long to saturate the sample with NO_x. Above 300 °C during both direct H_2 and WGS-assisted feed gas exposure, NO is completely converted. The complete conversion of NO shows that a sufficiently high number of sites active for NO dissociation are accessible. Since no NO_2 or N_2O formation is detected at these temperatures, a change in selectivity must occur. The selectivity towards NH_3 is likely suppressed by slow reaction between adsorbed N or NH_x species and adsorbed H atoms or by too low hydrogen coverage. The change in selectivity can be due to charge transfer from barium to palladium, affecting the electronic properties of Pd as a result of barium addition. This has been observed for Pd catalysts both under reducing [33] and oxidizing conditions[34] and may also be valid for the Ce-modified sample.

Interestingly, the lower NH_3 formation observed over the Ba- and Ce-modified samples during the temperature programmed reaction of NO + H_2 was not observed to the same extent during the transient lean/rich switching experiments. For most cases (with the exception of low-temperature conditions) these samples now exhibit behaviour similar to that of the Pd/Al_2O_3 reference sample. The short, excessively lean pulses employed during this experiment means that conditions are not as strongly reducing as those present in the temperature programmed experiment. Hence, it can be assumed that kinetic effects due to SMSI, as discussed above, are less pronounced resulting in higher NH_3 formation. The positive effect of lean/rich cycling over these samples is interesting and, since the concept of passive-SCR depends on a delicate type of operational switching between different gas stoichiometries, it may be of interest to further investigate the effect of transients over this sample. Since relatively long (four minutes) pulses were chosen in the present investigation, shortening the lengths of pulses or having a longer lean period compared to the rich one may further increase the activity for NH_3 formation over this formulation.

The NO_x storage properties of the BaO component were observed when H_2 was used directly in the feed gas during the transient lean/rich switching experiments. Evidence for the storage of NO during lean pulses is the delay in time before 500 ppm NO was detected by the FTIR (not displayed) which is not seen for the reference and cerium-doped samples. The time delay

15

observed is approximately 200 s and can be considered as the period required for total surface saturation to take place; NO is oxidized on the palladium sites prior to storage in the form of nitrates on the BaO phase. Subsequently, when O_2 is removed from the feed and conditions are rich again, the stored nitrates are reduced by the supplied H_2 [35, 36]. This explains the slight increase in NH_3 formation activity observed when a switch from lean to rich conditions is initiated. After a short time, the stored NO_x supply is depleted and the NH_3 formation activity over the Ba-modified sample reaches steady state. No NO_x storage was observed during the WGS-assisted transient reactions, explaining why there is no initial peak production of NH_3 when switches to rich conditions are employed.

With regards to the Ce-modified sample, an interesting observation of this sample in the presence of NO + H_2 is the ability to temporarily form low amounts of NH_3 in the presence of slightly oxidizing global conditions at low temperature. Although this effect is not yet understood, the experiment has been repeated and the results confirmed. Thus, this phenomenon is an area of interest for future research and is most likely to be related to the oxygen storage capacity of the ceria. In the experimental protocol conducted, the oxygen feed was decreased stepwise in terms of concentration, starting from a large excess of that required for stoichiometric conditions to be met. Thus, when exposed to the first stoichiometric value at which the formation of low amounts of ammonia is observed (S = 1.53), this may indicate the concentration at which the ceria is able to buffer the oxygen slightly, extending the period required for total oxidation of the sample to take place. This is suggested because a near but not fully steady-state response regarding the formed NH_3 is reached over these globally lean points, which may indicate that some active sites of the sample are exposed to a locally reducing environment due to the unique oxygen storage properties of ceria. If these steps however, were allowed to reach steady-state as a result of extended periods of time under oxidizing conditions, the oxygen storage capacity of the ceria will likely diminish and the palladium sites subsequently become oxidized, which may result in a loss of activity for ammonia formation. As the purpose of the present investigation is to investigate potential catalyst formulations suitable for passive-SCR automotive applications, better fuel economy can be achieved if NH_3 can indeed be formed under stoichiometric or, even

better, slightly oxidizing global conditions rather than more rich conditions.

A substantial benefit from the impregnation of cerium is seen during all WGS-assisted NH_3 formation experiments. This was expected as the superior WGS reaction properties of cerium are well reported in literature, though the majority of investigations have been conducted by using ceria as the support material. Here we show that the addition of merely 10 wt.% cerium into the catalyst formulation results in a significant increase in activity for NH_3 formation. As briefly mentioned in the introduction, the formation of oxygen vacancies within ceria allows for the rapid dissociation of water to take place prior to reaction with carbon monoxide that has been adsorbed on the Pd sites. In the case where Al_2O_3 is used as the support material and cerium is absent in the catalyst formulation, water activation is not as favourable. Kugai *et al.* [37] have compared the WGS activity of catalysts supported by ceria and alumina and suggest that the combination of noble metal and ceria support creates new active sites with improved H_2O activation behaviour than the reportedly monofunctional sites present when alumina is used as the carrier phase.

5. Conclusions

This study shows that, although the modification of Pd/Al_2O_3 with cerium and barium has no beneficial effect on the formation of NH_3 via NO and directly available H_2 during the temperature programmed experiments, the addition of cerium proves advantageous when H_2O is used as the hydrogen source. This can be justified by the enhanced water-gas-shift properties of ceria, thus providing higher concentrations of hydrogen available for ammonia formation compared to those samples without cerium. The cerium-modified sample also shows positive behaviour during the oxygen step experiments when H_2 is directly available in the feed gas. Namely, the formation of NH_3 is still substantial at stoichiometric and even slightly oxidizing global environments of the feed gas. This is suspected to be due to the oxygen storage capacity of the cerium component but requires further studies to be confirmed. It is important however, to keep in mind that this is most likely a temporary effect which is only observed in the presence of conditions which are still very close to stoichiometric operation. In automotive applications, lean operation would occur in

much longer pulses, with a much greater oxygen excess in order to conserve fuel economy. Thus, the absence of NH_3 formation over the Ce-modified sample during transient pulsing is a better representation of how this sample would behave in a real application. Although the impregnation with barium to the catalyst formulation did not affect the activity for NH_3 formation during static conditions in the presence of either feed gas mixure, it was interesting that cycling of the feed gas between lean and rich conditions resulted in improved activity for NH_3 formation. As reasonably long pulses were conducted in this paper, it may be of interest in the future to determine whether shortening the length of the pulses or even altering the balance between lean and rich operation would result in higher activity over this sample.

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7. References

[1] M. A. Gómez-García, V. Pitchon, and A. Kiennemann *Environ. Int.*, vol. 31, pp. 445–467, 2005.

[2] N. Macleod, R. Cropley, J. M. Keel, and R. M. Lambert *J. Catal.*, vol. 221, pp. 20–31, 2004.

[3] Y. Liu, M. P. Harold, and D. Luss *Appl. Catal. B: Environ.*, vol. 121, pp. 239–251, 2012.

[4] E. Fridell, M. Skoglundh, B. Westerberg, S. Johansson, and G. Smedler *J. Catal.*, vol. 183, pp. 196–209, 1999.

[5] S. M. Park, M.-Y. Kim, E. S. Kim, H.-S. Han, and G. Seo *Appl. Catal. A: Gen.*, vol. 395, pp. 120–128, 2011.

[6] A. Lindholm, N. Currier, J. Li, A. Yezerets, and L. Olsson *J. Catal.*, vol. 258, pp. 273–288, 2008.

[7] N. Macleod and R. M. Lambert *Appl. Catal. B: Environ.*, vol. 46, pp. 483–495, 2003.

[8] C. Ciardelli, I. Nova, E. Tronconi, D. Chatterdee, T. Burkhardt, and M. Weibel *Chem. Eng. Sci.*, vol. 62, pp. 5001–5006, 2007.

[9] P. Forzatti, L. Lietti, I. Nova, and E. Tronconi *Catal. Today*, vol. 151, pp. 202–211, 2010.

[10] P. R. Dasari, R. Muncrief, and M. P. Harold *Catal. Today*, vol. 184, pp. 43–53, 2012.

[11] N. V. Heeb, A.-M. Forss, S. Brühlmann, R. Lüscher, C. J. Saxer, and P. Hug *Atm. Environ*, vol. 40, pp. 5986–5997, 2006.

[12] T. D. Durbin, J. T. Pisano, T. Younglove, C. G. Sauer, S. H. Rhee, T. Huai, J. W. Miller, G. I. MacKay, A. M. Hochhauser, M. C. Ingham, R. A. Gorse, L. K. Beard, D. DiCicco, N. Thompson, R. J. Stradling, J. A. Rutherford, and J. P. Uihlein *Atmos. Environ.*, vol. 38, pp. 2699–2708, 2004.

[13] C. D. DiGulio, J. A. Pihl, J. E. Parks II, M. D. Amiridis, and T. J. Toops *Catal. Today*, vol. 231, pp. 33–45, 2014.

[14] V. Y. Prikhodko, J. E. Parks, J. A. Pihl, and T. J. Toops *SAE Int. J. Engines*, vol. 7, pp. 1235–1243, 2014.

[15] S. H. Oh and T. Triplett *Catal. Today*, vol. 231, pp. 22–32, 2014.

[16] L. Castoldi, I. Nova, L. Lietti, and P. Forzatti *Catal. Today*, vol. 96, pp. 43–52, 2004.

[17] J. A. Pihl, J. E. Parks, C. S. Daw, and T. W. Root *SAE Tech. Paper 2006-01-3441*, 2006.

[18] L. Cumaranatunge, S. S. Mulla, A. Yezerets, N. W. Currier, W. N. Delglass, and F. H. Ribeiro *J. Catal.*, vol. 246, pp. 29–34, 2007.

[19] R. D. Clayton, M. P. Harold, and V. Balakotaiah *Appl. Catal. B: Environ.*, vol. 84, pp. 616–630, 2008.

[20] N. W. Cant, D. C. Chambers, and I. O. Y. Liu *Appl. Catal. B: Environ*, vol. 46, pp. 551–559, 2003.

[21] B. Perada-Ayo, U. De La Torre, and J. R. González-Marcos, M P amd González-Velasco *Catal. Today*, vol. 241, pp. 133–142, 2015.

[22] V. M. Shinde and G. Madras *Appl. Catal. B: Environ*, vol. 123-124, pp. 367–378, 2012.

[23] E. C. Adams, M. Skoglundh, M. Folic, E. C. Bendixen, P. Garbrielsson, and P.-A. Carlsson *Appl. Catal. B: Environ*, vol. 165, pp. 10–19, 2015.

[24] J. Dawody, M. Skoglundh, S. Wall, and E. Fridell *J. Mol. Catal. A*, vol. 225, pp. 259–269, 2005.

[25] S. Brunauer, P. H. Emmett, and E. Teller *J. Am. Chem. Soc.*, vol. 60, pp. 309–319, 1938.

[26] H. Kannisto, X. Karatzas, J. Edvardsson, L. J. Pettersson, and H. H. Ingelston *Appl. Catal. B: Environ.*, vol. 104, pp. 74–83, 2011.

[27] J. C. Summers and K. Baron *J. Catal.*, vol. 57, pp. 380–389, 1979.

[28] A. M. Márquez and J. F. Sanz *Appl. Surf. Sci.*, vol. 238, pp. 82–85, 2004.

[29] H. G. Stenger Jr and J. S. Hepburn *Energy Fuels 1*, vol. 5, pp. 412–416, 1987.

[30] T. P. Kobylinski and B. W. Taylor *J. Catal.*, vol. 33, pp. 376–384, 1974.

[31] V. Labalme, N. Benhamou, N. Guilhaume, E. Garbowski, and M. Primet *Appl. Catal. A: Gen*, vol. 133, pp. 351–366, 1995.

[32] X. Wang, D. H. Kim, J. H. Kwak, C. Wang, J. Szanji, and C. H. F. Peden *Catal. Today*, vol. 175, pp. 78–82, 2011.

[33] D. T. Wickham, B. W. Logsdon, and S. W. Cowley *J. Catal.*, vol. 128, pp. 198–209, 1991.

[34] F. Klingstedt, H. Karhu, A. Kalantar Neyestanaki, L.-E. Lindors, T. Salmi, and J. Vayrynen *J. Catal.*, vol. 206, pp. 248–262, 2002.

[35] T. Kobayashi, T. Yamada, and K. Kayano *SAE Tech. Paper 970745*, 1997.

[36] S. Matsumoto *Cattech*, vol. 4, pp. 102–109, 2000.

[37] J. Kugai, E. B. Fox, and C. Song *Appl. Catal. A: Gen*, vol. 456, pp. 204–214, 2013.