

# Ammonia formation over supported platinum and palladium catalysts for passive SCR applications

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## Introduction

Selective catalytic reduction (SCR) of nitrogen oxides (NO<sub>x</sub>) with ammonia from urea is a well-established technique for removing NO<sub>x</sub> from the exhaust of heavy-duty vehicles in the presence of excess oxygen<sup>1</sup>. However, it may be considered undesirable to implement this technology into passenger vehicles since the required urea storage system is costly to produce, increases the weight of the vehicle and requires refueling<sup>2</sup>. In the present work, we have investigated different catalyst formulations that under rich conditions may enable on-board formation of NH<sub>3</sub> by using NO and hydrogen sources that are readily available in the exhaust stream. The formed NH<sub>3</sub> could be stored on an SCR catalyst placed downstream and used as a NO<sub>x</sub> reductant during lean operation. This method, which is termed passive SCR and presently considered for both petrol and diesel fuelled vehicles, may result in a reduced dependence or even complete removal of the urea storage tank within the vehicle.

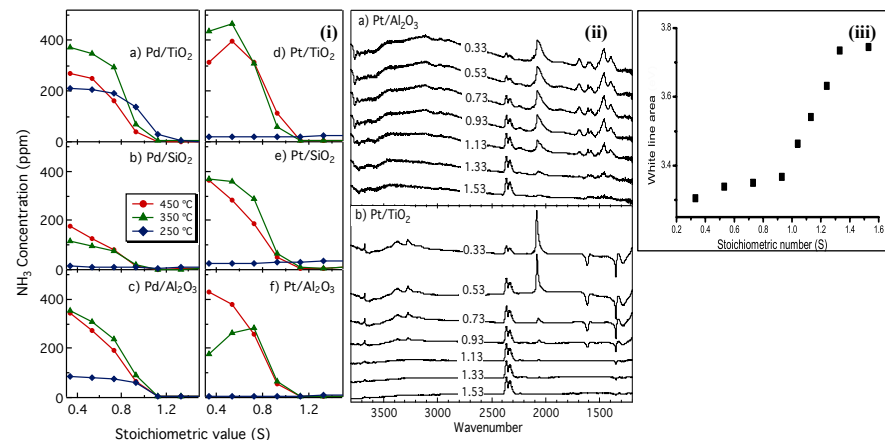
## Materials and Methods

A series of six powder catalysts (platinum or palladium supported on either alumina, silica or titania) were prepared via incipient wetness impregnation<sup>3</sup>. The powder catalysts were then coated onto monoliths for use in a gas flow reactor. In order to determine whether hydrogen formed via the water-gas-shift (WGS) reaction is a viable option for NH<sub>3</sub> formation, the gas feed consisted of NO, CO and H<sub>2</sub>O. To study the effect of oxygen, concentrations between 0 and 1050 ppm were fed to the reactor. This is represented in the form of the stoichiometric value of the gas feed, where  $S = (2[O_2] + [NO]) / [CO]$ . In order to obtain mechanistic information about the oxygen effect, the reaction scheme previously outlined was repeated on powder catalysts using *in situ* FTIR in diffuse reflectance mode. *In situ* XANES and EXAFS experiments were also conducted over Pt/Al<sub>2</sub>O<sub>3</sub> to determine the effect that oxygen has on platinum during the reaction of NO with H<sub>2</sub>.

## Results and Discussion

Figure 1-i shows the steady-state formation of NH<sub>3</sub> over the monolith catalysts during the gas flow reactor studies. It can be seen that NH<sub>3</sub> begins to form over all catalyst formulations when the gas feed is net-reducing ( $S < 1$ ). Only those samples which contain Pd are active for NH<sub>3</sub> formation at 250 °C since the WGS reaction is active over Pd at low temperature. However, upon reaching higher temperatures, the Pt-containing samples are able to form more elevated concentrations of NH<sub>3</sub> when compared to their Pd counterparts. It can also be seen that in some cases (most observable over Pt samples) the availability of very low oxygen concentration enhances NH<sub>3</sub> formation as compared to complete absence. This trend is also seen when hydrogen is directly available in the gas feed (not displayed in this abstract) and is most obvious over TiO<sub>2</sub> supported catalysts. It can be seen in figure 1-ii, which displays the *in situ* FTIR results, that as the gas feed tends towards lower stoichiometric values (lower oxygen concentrations) the band corresponding to the NH stretch

region increases in intensity. This is accompanied by a reduction in the contribution from gaseous CO<sub>2</sub> and, inversely, an increase in the adsorption of CO. This implies that CO oxidation occurs as a side-reaction when oxygen is present in the feed. This will limit the amount of hydrogen which can be formed via the WGS reaction and hence inhibit the formation of NH<sub>3</sub>. Since water and NH<sub>3</sub> overlap in the IR spectra, the oxidation of hydrogen itself cannot be excluded.



**Figure 1.** (i) Steady-state formation of NH<sub>3</sub> versus the stoichiometric value of the gas feed at 250, 350 and 450 °C obtained in the gas flow reactor (Ar balance, GHSV = 40 000h<sup>-1</sup>). (ii) Steady-state DRIFT spectra acquired at varying stoichiometric values of gas feed (values displayed on spectra). (iii) Whiteline area of the Pt L<sub>III</sub> edge during *in situ* XANES experiment at 350 °C versus varying stoichiometric feed gas values

Figure 1-iii shows the whiteline area of the Pt L<sub>III</sub> edge from *in situ* XANES during reaction of NO + H<sub>2</sub> over Pt/Al<sub>2</sub>O<sub>3</sub> as a function of the stoichiometric value of the gas feed. It can be seen that as the gas feed tends towards stoichiometric conditions ( $S=1$ ), there is a small but steady increase in Pt-oxides. However, once the gas feed becomes net-oxidizing, the intensity of the signal representing Pt-oxides increases rapidly and begins to level off when  $S=1.33$ . This may be due to the concentration of O<sub>2</sub> present in the gas feed being in excess of that required for total oxidation of the H<sub>2</sub>.

## Significance

Passive SCR is a newly emerging technique of after-treatment and this basic investigation has successfully shown that it is possible to form significant concentrations of NH<sub>3</sub> using NO and H<sub>2</sub>O although the effect of oxygen is one that must be addressed in future work.

## References

1. Balle P, Geiger B et al. Appl. Catal B 2009, 91, 587-595
2. Macleod N, Cropley R et al. Journal of Catalysis 2004, 221, 20–31.
3. Bounechada D, Fouladvand S et al. Phys. Chem. Chem. Phys. 2013, 15, 8648-8661