In situ ammonia generation as a strategy for catalytic NOx reduction under oxygen rich conditions

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Under highly oxygen rich conditions palladium/alumina catalysts exhibit strongly enhanced NOx reduction activity in the presence of CO:H$_2$ mixtures due to *in situ* generation of ammonia *via* the formation and subsequent hydrolysis of isocyanate (NCO) species.

Achieving catalytic reduction of NO$_x$ (NO + NO$_2$) in the presence of excess oxygen is of major environmental and economic importance, especially with respect to abatement of NO$_x$ emissions generated by fuel-efficient diesel and lean burn gasoline engines.[1] Both these engine types offer substantial improvements in fuel economy, hence lower CO$_2$ emission, compared to conventional gasoline engines. However, as they operate under fuel lean conditions, the presence of a very large excess of oxygen in the exhaust stream makes catalytic elimination of NO$_x$ extremely difficult.

The most convenient strategy for NO$_x$ removal involves exploitation of the reducing agents that are already present in the gas stream, namely hydrocarbons, CO and hydrogen. Platinum-based catalysts in particular have been extensively studied in recent years, and although they are amongst the most active in NO$_x$ reduction by hydrocarbons,[2] their catalytic performance remains inadequate for practical application under lean conditions. In this respect, hydrogen is more a promising reductant, delivering NO$_x$ conversions significantly higher than those attainable with hydrocarbons.[3] Hydrogen has the added advantage of being an effective reductant at much lower temperatures than hydrocarbons. However, platinum-catalysed NO$_x$ reduction with hydrogen suffers from important drawbacks. First, selectivity is low, tending to produce more N$_2$O (a powerful greenhouse gas) than N$_2$. Second, the hydrogen content in lean engine exhausts is closely linked to the CO concentration, the typical H$_2$:CO ratio being ~ 1:3. This high content of strongly-adsorbing CO leads to extensive poisoning of platinum-based catalysts.[4,5]

Recently we reported on the performance of palladium/Al$_2$O$_3$ based catalysts under lean conditions in the presence of mixed H$_2$:CO reductant feeds.[5,6] In this case it was found that, far from acting as a poison, CO actually *promotes* NO$_x$ reduction. Close to 100% NO conversion was obtained at a 100:1 O$_2$:NO ratio, with good N$_2$ selectivity (70%) and at low temperature (150 °C). However the mechanism responsible for this remarkable behaviour was unexplained.

Now we are able to report *in situ* infra-red spectroscopic observations on the surface species present under reaction conditions. These results reveal a new mechanism for NO$_x$ reduction, apparently specific to palladium surfaces. This involves formation of isocyanate, its subsequent hydrolysis to ammonia, followed by reaction of the latter with NO$_x$. In effect, we have a catalytic system whose intrinsic chemistry internally generates NH$_3$, a powerful NO$_x$ reductant. (Recall that injection of NH$_3$ from an external supply is the strategy used for NO$_x$ elimination from stationary sources.[7])

Evidence for the formation of NH$_3$ on the catalyst surface under reaction conditions is shown in Figure 1. These *in situ* DRIFTS† spectra were obtained at 150 °C (reaction temperature) with a Pd/Al$_2$O$_3$ catalyst. The O–H and N–H stretching frequency region is displayed. In this experiment the

gas feed to the DRIFTS cell was switched from 4000 ppm H$_2$ + 500 ppm NO +5% O$_2$ to a feed containing *1000 ppm CO* + 3000 ppm H$_2$ + 500 ppm NO + 5% O$_2$. Addition of CO produced a dramatic improvement in NO$_x$ conversion and the resulting time dependent changes in the diffuse reflectance spectra are shown in Figure 1. Bands developed at 3254 cm^{-1} and 3176 cm^{-1} (shoulder), which are assigned to N–H stretching modes of adsorbed NH$_3$.[8] The growing negative peak at 3720 cm^{-1} is also diagnostic of NH$_3$. It results from eradication of free O–H groups on the alumina surface by H-bonding interaction with adsorbed ammonia.[8] *It is important to note that in the absence of CO no evidence for the presence of ammonia was obtained.*

The most likely route involving CO participation in NH$_3$ formation is *via* the intermediacy of isocyanate:

$$NO + CO \rightarrow NCO \tag{1}$$

$$NCO + H_2O \rightarrow NH_3 + CO_2 \tag{2}$$
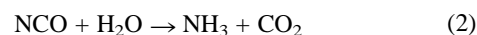
NCO is not detected under the conditions employed in Figure 1, probably due to its high reactivity and low steady state coverage under full reaction conditions.

Figure 2 illustrates that this is indeed the case. Here, at 150 °C, exposure of the catalyst to 4000 ppm CO + 500 ppm NO + 5% O$_2$ *in the absence of H$_2$* (Figure 2**a**) led to build up of adsorbed NCO as shown by the appearance of bands at 2257 and 2233 cm^{-1}. Isocyanate is formed on the palladium particles, followed by spill-over onto the alumina support where it accumulates.[9] The appearance of two isocyanate bands is ascribed to two different modes of NCO adsorption on the alumina surface.[10] (In an identical experiment performed with a *platinum*/alumina catalyst no NCO was observed. This is highly significant, as CO poisons rather than promotes such catalysts. We have also found rhodium catalysts to be ineffective under these conditions.) The remaining bands in Figure 2**a** are assigned to CO adsorbed on palladium sites. The bands at 2158 cm^{-1} and 2080 cm^{-1} are assigned to linear Pd$^+$–CO and Pd^0–CO species respectively, whilst the 1975 cm^{-1} and 1911 cm^{-1} bands are assigned to bridged and threefold bonded CO respectively.[11]
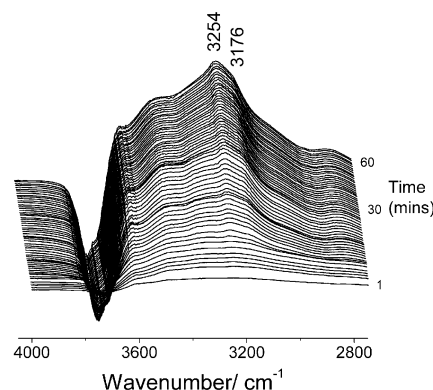

Fig. 1 Time resolved DRIFT spectra obtained over a palladium catalyst at 150 °C following switch in gas feed from 4000 ppm H$_2$ + 500 ppm NO + 5% O$_2$ to 3000 ppm H$_2$ + 1000 ppm CO + 500 ppm O$_2$ + 5% O$_2$.

The reactivity of accumulated NCO under two different conditions was studied. First, by interrupting the CO feed, thus subjecting the isocyanate to a flow of 500 ppm NO + 5% O_2 alone. As shown in Figure 2**b**, the NCO species were relatively stable in this environment, a gradual loss in intensity of the isocyanate bands occurring over time. (Significant intensity remained 1 hour after the gas switch.) Second, by switching in hydrogen to replace CO (*4000 ppm H_2 + 500 ppm NO + 5% O_2*). In this case NCO was rapidly destroyed (Figure 2**c**) the associated bands being totally extinguished within three minutes. The most likely explanation for this high reactivity of NCO in the presence of H_2 + O_2 is its rapid hydrolysis to NH_3 and CO_2 [Equation (2)]. This is consistent with its undetectably low steady state coverage in H_2 + CO containing reaction gas, whereas the hydrolysis product *is* detectable (Figure 1).

It is however clear that the role of hydrogen in this system is not restricted merely to generation of H_2O for NCO hydrolysis. Thus the high NO_x conversions obtained in the presence of H_2 + CO were not reproduced when H_2 was replaced by water. A possible explanation for this difference is as follows. Formation of NCO on the Pd surface occurs by reaction of CO(a) with N(a). N(a) is formed by NO dissociation, the likely rate determining step under these conditions of high CO coverage.[12] It is therefore significant that all bands associated with palladium-bound CO species were significantly red-shifted in the presence of hydrogen, as shown in Figure 3. This is reasonably attributed to electron-donation from H(a) to palladium resulting in increased d $\rightarrow$ π^* back donation thus weakening of the C–O bond.[13] The same effect of co-adsorbed H(a) is to be expected with NO(a). This would significantly increase the rate of NO dissociation and hence the rate of NCO formation, in line with our findings. Indeed, greatly enhanced rates of NO dissociation in the presence of H_2 have been reported previously.[14]

Although NH_3 (and NCO) formation has been observed previously on a variety of different catalysts tested with these applications in mind, its generation has not previously been reported with this technically relevant combination of reductants and, more importantly, at these low temperatures. It is
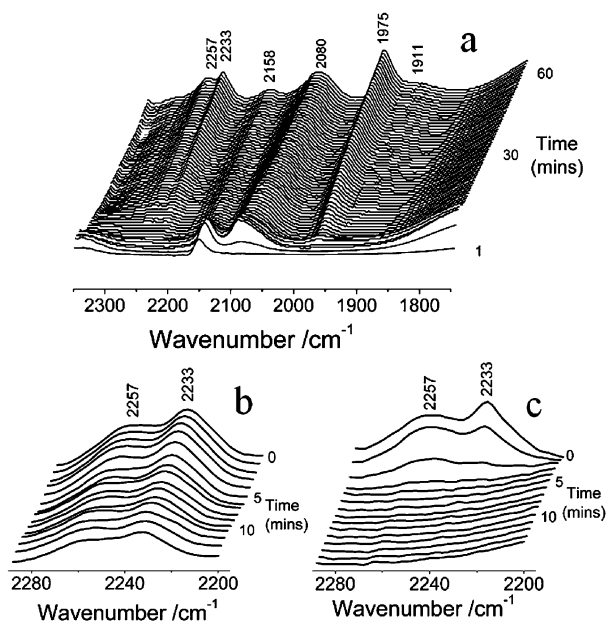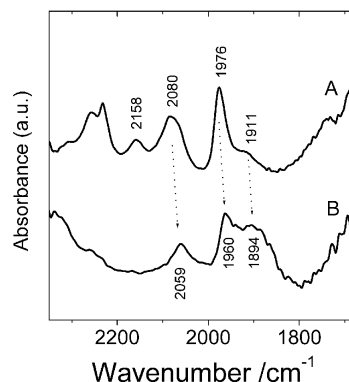

Fig. 3 Comparison of adsorbed CO stretching frequencies in various gas atmospheres; **A**, 4000 ppm CO + 500 ppm NO + 5% O_2; **B**, 1000 ppm H_2 + 3000 ppm CO + 500 ppm NO + 5% O_2.

likely that low temperature operation actually contributes to the high NO_x conversions observed, as at higher temperatures direct combustion of the reductants by oxygen is favoured.

In conclusion, we have shown that under demanding conditions (low temperature, high oxygen excess) palladium/alumina catalysts in the presence of H_2 + CO deliver greatly improved NO_x reduction due to *in situ* generation and subsequent reaction of NH_3 species. It is likely that identification of suitable promoters would lead to new formulations with further improved catalytic properties. Therefore we believe this system represents a promising new strategy for the control of NO_x emissions generated under oxygen rich conditions.

Notes and references

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Fig. 2 Formation and reactivity of NCO species (see text for details).