

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

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Under highly oxygen rich conditions palladium/alumina catalysts exhibit strongly enhanced NO_x reduction activity in the presence of CO:H₂ 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 + NO₂) 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 CO₂ 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 N₂O (a powerful greenhouse gas) than N₂. Second, the hydrogen content in lean engine exhausts is closely linked to the CO concentration, the typical H₂:CO ratio being ~ 1:3. This high content of strongly-adsorbing CO leads to extensive poisoning of platinum-based catalysts.^{4,5}

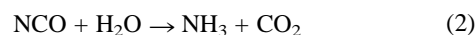
Recently we reported on the performance of palladium/Al₂O₃ based catalysts under lean conditions in the presence of mixed H₂:CO reductant feeds.^{5,6} In this case it was found that, far from acting as a poison, CO actually *promotes* NO_x reduction. Close to 100% NO conversion was obtained at a 100:1 O₂:NO ratio, with good N₂ 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 NH₃, a powerful NO_x reductant. (Recall that injection of NH₃ from an external supply is the strategy used for NO_x elimination from stationary sources.⁷)

Evidence for the formation of NH₃ 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/Al₂O₃ 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 H₂ + 500 ppm NO + 5% O₂ to a feed containing 1000 ppm CO + 3000 ppm H₂ + 500 ppm NO + 5% O₂. 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 NH₃.⁸ The growing negative peak at 3720 cm⁻¹ is also diagnostic of NH₃. 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 NH₃ formation is *via* the intermediacy of isocyanate:



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% O₂ in the *absence* of H₂ (Figure 2a) 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 2a 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 Pd⁰–CO species respectively, whilst the 1975 cm⁻¹ and 1911 cm⁻¹ bands are assigned to bridged and threefold bonded CO respectively.¹¹

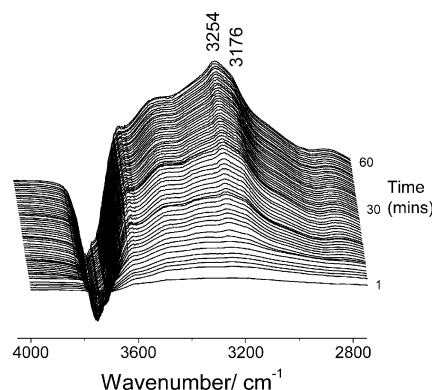


Fig. 1 Time resolved DRIFT spectra obtained over a palladium catalyst at 150 °C following switch in gas feed from 4000 ppm H₂ + 500 ppm NO + 5% O₂ to 3000 ppm H₂ + 1000 ppm CO + 500 ppm O₂ + 5% O₂.

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% O₂ alone. As shown in Figure 2b, 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 H₂ + 500 ppm NO + 5% O₂). In this case NCO was rapidly destroyed (Figure 2c) the associated bands being totally extinguished within three minutes. The most likely explanation for this high reactivity of NCO in the presence of H₂ + O₂ is its rapid hydrolysis to NH₃ and CO₂ [Equation (2)]. This is consistent with its undetectably low steady state coverage in H₂ + 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 H₂O for NCO hydrolysis. Thus the high NO_x conversions obtained in the presence of H₂ + CO were not reproduced when H₂ 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 → 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 H₂ have been reported previously.¹⁴

Although NH₃ (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

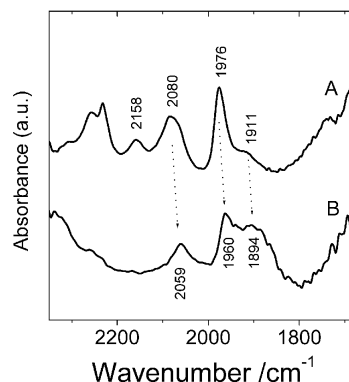


Fig. 3 Comparison of adsorbed CO stretching frequencies in various gas atmospheres; **A**, 4000 ppm CO + 500 ppm NO + 5% O₂; **B**, 1000 ppm H₂ + 3000 ppm CO + 500 ppm NO + 5% O₂.

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 H₂ + CO deliver greatly improved NO_x reduction due to *in situ* generation and subsequent reaction of NH₃ 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

† DRIFTS experiments were performed with a Perkin-Elmer GX2000 spectrometer equipped with an MCT detector and a high temperature DRIFTS cell (Thermo Spectra-Tech) fitted with ZnSe windows. Spectra were acquired at a resolution of 4 cm⁻¹ typically averaging 64 scans.

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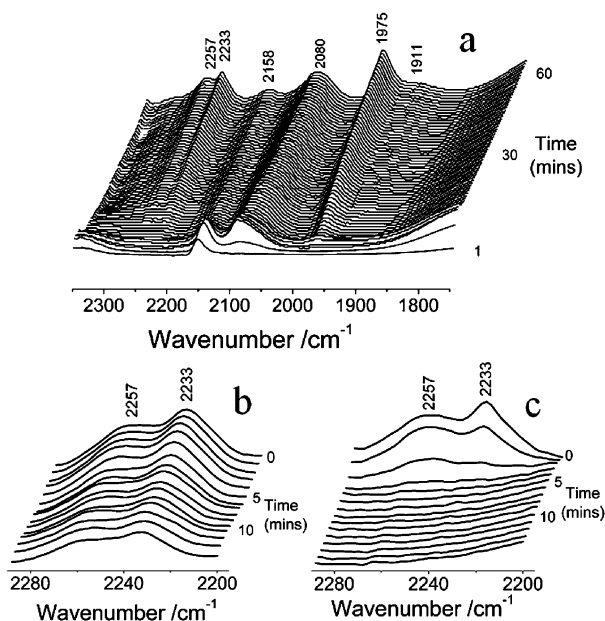


Fig. 2 Formation and reactivity of NCO species (see text for details).