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# Exploiting the synergy of titania and alumina in lean NO<sub>x</sub> reduction: in situ ammonia generation during the Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-catalysed H<sub>2</sub>/CO/NO/O<sub>2</sub> reaction

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#### Abstract

In situ DRIFTS, XPS, HREM, XRD, and reactor studies have been used to examine and elucidate the catalytic performance of Pd particles supported on TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. These materials deliver 100% NO<sub>x</sub> conversion under demanding and technically relevant conditions (low temperature, high oxygen excess) in the presence of mixed  $H_2$  + CO reductant feeds. In particular, they are far superior to the corresponding Pd/TiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts. It is shown that the synergy that operates between the titania and the alumina components involves the intrinsic surface chemistry of these oxides rather than formation of mixed oxide phases. Specifically, titania is critical for the formation of NCO on Pd while alumina promotes subsequent hydrolysis of NCO to ammonia, which then reduces NO<sub>x</sub>. At high temperature a second NO<sub>x</sub> reduction channel operates with Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> which greatly extends the useful temperature range. This also involves in situ formation of ammonia—in this case directly from reaction between H<sub>2</sub> and NO.

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#### 1. Introduction

The exhaust streams generated by diesel and lean burn gasoline engines and stationary power plants contain very high background oxygen levels, making effective utilisation of any reductant species present for catalytic reduction of the nitrogen oxides produced extremely difficult [1–4]. The environmental consequences arising due to release of these NO<sub>x</sub> (NO + NO<sub>2</sub>) species have been well documented (acid rain, photochemical smog, depletion of stratospheric ozone). The lack of an effective catalyst/reductant combination for this process is one of the main obstacles preventing widespread introduction of fuel-efficient lean burn engines, which have the potential to significantly reduce the global CO<sub>2</sub> burden.

For stationary power sources and chemical plants the NH<sub>3</sub> SCR process [3,4] is currently the preferred option for NO<sub>x</sub> abatement. Ammonia is utilised due to its unique high activity toward NO<sub>x</sub> reduction under these oxygen-rich

\* Corresponding author. *E-mail address:* rml1@cam.ac.uk (R.M. Lambert). conditions. Although this process is very effective, the requirement for a  $NH_3$  reservoir and injection system makes use of this technology problematic for transport applications. Safer alternatives such as urea [5–7], which can be used to generate  $NH_3$  in situ, add further complexity and cost.

Recently we identified a number of palladium-based catalysts that generate  $NH_3$  in situ when fed with  $H_2/CO/NO$  mixtures in the presence of very high oxygen concentrations. Hydrogen and CO are both frequently encountered in the exhaust streams produced by hydrocarbon combustion processes; therefore, this strategy could potentially remove the requirement for injection of additional reductant into the exhaust. Two separate systems capable of in situ  $NH_3$  generation have been identified.

Thus Pd/Al<sub>2</sub>O<sub>3</sub> catalysts fed with  $H_2 + CO + NO + O_2$ reactant streams at relevant partial pressures exhibited much improved performance compared to the results obtained with either  $H_2$  or CO used alone [8–10]. In situ DRIFTS studies revealed that this improvement in the NO<sub>x</sub> conversion was attributable to the generation of ammonia formed via the production and subsequent hydrolysis of isocyanate (NCO) species [9]. This increase in NO<sub>x</sub> conversion obtained in the presence of mixed  $H_2 + CO$  reductant feeds is signifi-

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cant as the  $H_2$  and CO concentrations in exhaust streams are closely linked due to equilibration via the water gas-shift reaction.

Pd/TiO<sub>2</sub> catalysts, on the other hand, display very high activity for the reduction of lean  $NO_x$  in the absence of CO, i.e., with  $H_2 + NO + O_2$  mixtures [11–13]. These catalysts are active in two distinct temperature regimes, indicating operation of two different mechanisms for  $NO_x$  reduction. By means of in situ DRIFTS we were able to attribute the lower temperature (~110 °C) NO<sub>x</sub> reduction channel to a mechanism involving dissociation of NO on reduced metal  $(Pd^0)$  sites [13]. The second, higher temperature (~250 °C),  $NO_x$  reduction channel operated via formation and subsequent reaction of NH<sub>3</sub> [13], in this case generated directly by reaction of H<sub>2</sub> with NO. While the low temperature channel operated over a rather narrow temperature region  $(\sim 100-130 \,^{\circ}\text{C})$ , the NH<sub>3</sub>-driven channel maintained NO<sub>x</sub> conversions > 50% over a much wider temperature range (200-280°C).

Here we are concerned with the effects of CO. Specifically, we report on the  $H_2 + CO + NO + O_2$  reaction over Pd/TiO<sub>2</sub> and Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts. Our aim was to identify the reason for the improved performance of the mixed support catalyst Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> [14] compared to Pd/TiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub> under the same conditions. Detailed characterisation of the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> support has been performed which, combined with in situ DRIFTS results, has enabled us to elucidate aspects of the reaction mechanism.

#### 2. Experimental

Mixed TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> supports, with varying TiO<sub>2</sub> loadings, were prepared by hydrolysis of titanium isopropoxide in the presence of a  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (Aldrich, 120 m<sup>2</sup>/g). The resulting solid materials were dried and calcined in flowing air for 10 h at 500 °C. Palladium was subsequently impregnated by incipient wetness using aqueous solutions of palladium(II)nitrate (Aldrich) to yield 0.5 wt% metal loading. Following impregnation the catalysts were dried in air overnight at 110 °C, calcined in air at 500 °C for 6 h, and subsequently crushed/sieved to yield grain sizes in the range 255–350  $\mu$ m. The 0.5 wt% Pd/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and 0.5 wt% Pd/TiO<sub>2</sub> (Degussa P25) catalysts were prepared in a similar manner. Metal dispersion was determined using the CO methanation technique [15]. Prior to this measurement the samples were calcined in air (60 ml min<sup>-1</sup>) for 6 h at 500 °C followed by reduction in H<sub>2</sub> (60 ml min<sup>-1</sup>) for 1 h at 150 °C. Metal dispersions were calculated assuming a 1:1 CO to surface metal atom ratio.

Powder XRD patterns were obtained on a Philips PW1710 instrument employing Cu-K<sub> $\alpha$ </sub> radiation. Transmission electron microscopy was performed on a JOEL 3011 microscope operating at 300 kV and equipped with a Princeton Gamma-Tech energy dispersive X-ray spectrometer. XPS was per-

formed on a VSW ARIES system equipped with a HA-100 hemispherical analyser. Catalyst samples were mounted by pressing a small amount of the material between two disks of pure aluminum. Separating the disks produced two specimens consisting of a thin film of catalyst powder adhering to the aluminum. XP spectra were acquired with Mg-K<sub> $\alpha$ </sub> radiation and quoted binding energies (BEs) are referred to the C 1s emission at 284 eV. The different contributions to the Ti 2p<sub>3/2, 1/2</sub> emission were extracted by curve fitting.

Catalyst testing was performed in a quartz microreactor system described previously [15]. The feed composition employed contained 5% O2 and 500 ppm NO in all cases with a total reductant concentration of 4000 ppm, delivered to the reactor with a total flow of 200 ml min<sup>-1</sup>. One hundred milligrams of sample was employed, corresponding to a reciprocal weight time velocity of  $w/f = 0.03 \text{ g s ml}^{-1}$ . Prior to testing the samples were calcined in air (60 ml min<sup>-1</sup>) for 6 h at 500 °C. The reactor outflow was analysed using a chemiluminescence  $NO_x$  (NO + NO<sub>2</sub>) detector (Signal 4000 series) and two dual-channel NDIR detectors (Siemens Ultramat 6) calibrated for CO/CO<sub>2</sub> and NO/N<sub>2</sub>O. Hydrogen consumption was monitored via a quadrupole mass spectrometer (Hiden RGA 301). Nitrogen production was calculated by subtracting the N<sub>2</sub>O contribution from the total  $NO_x$  conversion (GC analysis produced no evidence for NH<sub>3</sub> in the reactor outlet during these experiments). The catalyst temperature and all analyser outputs were continuously monitored and recorded by PC-based software. Conversion profiles, typically containing 1000 data points per channel, were obtained as the catalyst temperature was raised from 50 to  $450 \,^{\circ}$ C with a linear ramp of  $2 \,^{\circ}$ C min<sup>-1</sup>. These runs were repeated several times in order to ensure stable and reproducible performance. Temperature-programmed desorption (TPD) experiments were also performed in this system, employing a He flow of 150 ml min<sup>-1</sup> with a heating rate of 10 K min<sup>-1</sup>. The sample (100 mg) was initially heated to 500 °C in He, cooled to 50 °C, and subsequently dosed with a feed containing 500 ppm NO + 5%  $O_2$ . The TPD ramp was then performed between 50 and 550 °C. Desorption of NO/N2O was monitored by NDIR, NO2 by chemiluminescence, and O<sub>2</sub>/N<sub>2</sub> by mass spectrometry.

DRIFTS experiments were performed with a Perkin-Elmer GX2000 spectrometer equipped with an MCT detector and a high-pressure, high-temperature DRIFTS cell (Thermo Spectra-Tech) fitted with ZnSe windows. Spectra were acquired at a resolution of 4 cm<sup>-1</sup> typically averaging 64 scans. Background spectra were obtained from samples at the relevant temperature in a flow of helium, following identical pretreatment to that utilised in the reactor experiments. All spectra were taken after 1 h in the relevant gas mix unless otherwise stated. The flow rate through the DRIFT cell was varied so as to maintain conversions in the range 10–20%. Therefore the spectra displayed correspond to the state of the catalyst toward the front end of the sample bed in the tubular reactor.

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Table 1	
Palladium dispersion	

Sample	CO uptake (µmol/g <sub>cat</sub> )	Dispersion <sup>a</sup> (%)
0.5 wt% Pd/Al <sub>2</sub> O <sub>3</sub>	22.0	47
0.5 wt% Pd/TiO <sub>2</sub>	14.1	30
0.5 wt% Pd/2.5 wt% TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	19.2	41
0.5 wt% Pd/10 wt% TiO2/Al2O3	18.3	39
0.5 wt% Pd/25 wt% TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	12.7	27

<sup>a</sup> Assumes 1:1 CO to surface metal atom ratio.

## 3. Results

#### 3.1. Catalyst characterisation

Metal dispersion data for the Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, and various TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>-supported palladium samples are listed in Table 1. In general the metal dispersion varied in line with the total surface area, with the alumina-supported sample having a higher dispersion (47%) than that of TiO<sub>2</sub> (30%). For the mixed support catalysts the palladium dispersion decreased as the TiO<sub>2</sub> loading increased.

X-ray diffraction patterns obtained from Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts with varying TiO<sub>2</sub> loadings are shown in Fig. 1. These data were obtained after calcination of the samples in air at 500 °C for 6 h. The sample containing 2.5 wt% TiO<sub>2</sub> displayed a pattern identical to that of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support, indicating that the TiO<sub>2</sub> component was highly dispersed over the surface of the alumina. The same is true of the 10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> sample, although in this case weak reflections due to the anatase form of TiO<sub>2</sub> were also visible. On increasing the loading further to 25 wt% the intensity of the anatase reflections increased considerably, indicating an increase in the number and size of crystalline TiO<sub>2</sub> particles (line broadening analysis gave an average TiO<sub>2</sub> particle size of 10 nm for this sample). The 10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> sample was found to yield the best catalytic performance, and was therefore characterised in more detail by HREM/EDX, XPS, and TPD.



Fig. 1. Powder XRD patterns obtained from  $Pd/TiO_2/Al_2O_3$  catalysts with varying  $TiO_2$  loadings following calcination in air at 500 °C for 6 h.

HREM images obtained from this sample are shown in Fig. 2. A number of TiO<sub>2</sub> particles in the size range 2–5 nm were imaged, examples of which are shown. However, EDX analysis indicated that a significant proportion of the TiO<sub>2</sub> was present in a highly dispersed form, as spectra obtained from areas containing no visible TiO<sub>2</sub> particles (utilising a relatively large electron beam probe diameter,  $\sim$  50 nm) frequently displayed significant Ti peak intensity.

XPS spectra (Ti 2p) obtained from the 0.5 wt% Pd/TiO<sub>2</sub> and 0.5 wt% Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> samples are compared in Figs. 3a and 3b, respectively. In the case of the Pd/TiO<sub>2</sub> sample, the peak found at 459.2 eV is assigned to Ti<sup>4+</sup>. The corresponding oxygen peaks (not shown) were resolved into two species, one at 530.8 eV and a smaller peak a 531.6 eV, corresponding to oxygen in the bulk titania and oxygen from surface hydroxyl groups, respectively.



Fig. 2. HREM images obtained from the Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst showing presence of TiO<sub>2</sub> particles in the 2–5 nm size range.



Fig. 3. Ti 2p XP spectra obtained from (a) Pd/TiO\_2 and (b) Pd/10 wt% TiO\_2/Al\_2O\_3 samples.

The Ti(2p) peak obtained from the 10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> sample, shown in Fig. 3b, was significantly broader than that observed with Pd/TiO<sub>2</sub>, indicating the presence of multiple oxidation states. Curve fitting indicates the presence of Ti<sup>2+</sup> and Ti<sup>3+</sup> in addition to the dominant (90% of the total signal) Ti<sup>4+</sup> peak. The Ti:Al surface atomic ratio determined by XPS was estimated as ~ 1:3 for this sample. This is further evidence for the presence of a highly dispersed TiO<sub>2</sub> component, as the number density of 3D TiO<sub>2</sub> particles imaged by HREM was insufficient to give such a high Ti:Al ratio.

Temperature-programmed desorption spectra obtained from the 0.5 wt% Pd/Al<sub>2</sub>O<sub>3</sub>, 0.5 wt% Pd/TiO<sub>2</sub> (P25) and 0.5 wt% Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> samples following exposure to NO +  $O_2$  (500 ppm NO + 5%  $O_2$ ) at 50 °C are shown in Figs. 4a, 4b, and 4c, respectively. (The Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/TiO<sub>2</sub> profiles have been published previously [13] and are included here for the purpose of comparison with Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>.) The desorption spectra obtained from the Al<sub>2</sub>O<sub>3</sub> supported catalyst are dominated by two regimes, one centred at 150 °C and one at 390 °C. The low-temperature peaks are due to NO and NO<sub>2</sub>, while the high-temperature peaks are due to NO, NO<sub>2</sub>, and O<sub>2</sub>. A further small NO<sub>2</sub> desorption peak is visible at 290 °C. On the TiO<sub>2</sub> supported sample, Fig. 4b, two NO<sub>2</sub> desorption peaks were again observed (220 and 340 °C) along with an O<sub>2</sub> peak at 340 °C. A small NO desorption peak appeared at 150 °C but no



Fig. 4. Temperature-programmed desorption spectra obtained from (a)  $Pd/Al_2O_3$ , (b)  $Pd/TiO_2$ , and (c)  $Pd/10 \text{ wt}\% \text{ Ti}O_2/Al_2O_3$  catalysts following exposure to NO + O<sub>2</sub> at 50 °C. [NO] = 500 ppm, [O<sub>2</sub>] = 5%.

high-temperature NO desorption was observed in this case. However, the most important point to note from this TPD data is that in the case of the mixed  $TiO_2/Al_2O_3$  support, Fig. 4c, the desorption profiles obtained contain a combination of the features observed on the individual oxides. For example, the high-temperature NO peak at 420 °C is characteristic of alumina while the NO<sub>2</sub> desorption feature at 230 °C is associated with the TiO<sub>2</sub> component.

Corresponding DRIFT spectra were obtained at 50 K intervals. Fig. 5 displays an extract from this data set, showing spectra obtained from the Pd/TiO<sub>2</sub>, Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, and Pd/Al<sub>2</sub>O<sub>3</sub> samples at 250 °C. These spectra are simplified due to desorption of the majority of the nitrite species present at lower temperatures. Although significant overlap of various nitrate bands is still present, it is clear that the mixed support displays features characteristic of both constituent oxides. For example the intense peak at  $\sim 1618 \text{ cm}^{-1}$  observed on both titania-containing samples is assigned to the asymmetric stretching mode of a bridging nitrate species adsorbed on TiO<sub>2</sub> sites [16–18]. The corre-



Fig. 5. DRIFT spectra obtained with various supported Pd catalyst following exposure to NO +  $O_2$  flow at 50 °C and subsequent heating to 250 °C in flowing He. [NO] = 500 ppm, [ $O_2$ ] = 5%.

sponding symmetric stretch occurs at  $\sim 1230 \text{ cm}^{-1}$ . On the other hand the peak at 1303 cm<sup>-1</sup> observed on aluminacontaining samples is associated with the symmetric stretching mode of a bidentate nitrate adsorbed on alumina [19,20]. In this case the asymmetric stretch occurs at  $\sim 1563 \text{ cm}^{-1}$ . This observation that the surface of the mixed support contains adsorption sites characteristic of both alumina and titania components is important in relation to the catalytic properties discussed below.

#### 3.2. NO reduction by $H_2$

Conversion versus temperature profiles obtained during the reduction of NO by hydrogen (4000 ppm  $H_2 + 500$  ppm  $NO + 5\% O_2$ ) over the various supported palladium catalysts are shown in Fig. 6. As found previously [10,11], the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst displayed very low activity under these conditions, with the  $NO_x$  conversion remaining below 10% over the entire temperature range studied. In contrast with the Pd/TiO<sub>2</sub> catalyst, NO<sub>x</sub> conversions of  $\sim$  70% were achieved in two distinct temperature regimes. One centred at low temperature (110 °C), in the region were  $H_2$  conversion approaches 100%, and one at higher temperature (240 °C). The presence of two reduction maxima indicates operation of two distinct mechanisms for  $NO_x$  reduction over this catalyst as noted previously by Ueda et al. [11,12]. Although the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst was relatively inactive, when modified by the addition of TiO<sub>2</sub> the sample displayed much improved performance, achieving NO<sub>x</sub> conversions of  $\sim$  50% in both temperature regimes.

Fig. 7 shows the corresponding DRIFT spectra obtained under identical conditions (4000 ppm H<sub>2</sub> + 500 ppm NO + 5% O<sub>2</sub>) at 120 °C: this temperature corresponds to the lowtemperature NO<sub>x</sub> reduction pathway shown in Fig. 6. At this temperature, Pd/Al<sub>2</sub>O<sub>3</sub> showed bands due to adsorbed



Fig. 6. Conversion profiles for (a) hydrogen and (b) NO<sub>x</sub> as a function of temperature over various palladium-containing catalysts. [H<sub>2</sub>] = 4000 ppm, [NO] = 500 ppm, [O<sub>2</sub>] = 5%, w/f = 0.03 g s ml<sup>-1</sup>.



Fig. 7. DRIFT spectra obtained with various supported palladium catalysts in flowing  $H_2 + NO + O_2$  at 120 °C.  $[H_2] = 4000$  ppm, [NO] = 500 ppm,  $[O_2] = 5\%$ .



Fig. 8. DRIFT spectra obtained with various supported palladium catalysts in flowing  $H_2 + NO + O_2$  at 240 °C. [H<sub>2</sub>] = 4000 ppm, [NO] = 500 ppm, [O<sub>2</sub>] = 5%.

water (1644 cm<sup>-1</sup>) and hydrated nitrate species (1403 and 1327 cm<sup>-1</sup> [21]). No evidence for the presence of Pd nitrosyl species was found with this catalyst. In contrast, under these conditions the Pd/TiO<sub>2</sub> catalyst gave bands that may be assigned to Pd<sup>2+</sup>–NO (1842 cm<sup>-1</sup>), Pd<sup>+</sup>–NO (1787 cm<sup>-1</sup>), Pd<sup>0</sup>–NO (1722 cm<sup>-1</sup>), and a bent Pd nitrosyl species (1693 cm<sup>-1</sup>) [13,22–30]. The remaining bands in this spectrum are assigned to variously TiO<sub>2</sub> coordinated nitrates. Over the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> sample a broad peak was observed in the nitrosyl region centred at 1795 cm<sup>-1</sup>. The broad and asymmetric nature of this peak indicates adsorption of NO on a range of different palladium sites (Pd<sup>+</sup> and Pd<sup>0</sup>).

The corresponding spectra obtained at 240 °C are shown in Fig. 8. This temperature corresponds to the high-temperature  $NO_x$  reduction pathway apparent in Fig. 6. The Pd/ Al<sub>2</sub>O<sub>3</sub> spectrum shows bands due to anhydrous nitrates due to desorption of the water present at the lower temperature. On the Pd/TiO2 sample, in addition to nitrates, evidence for the presence of adsorbed NH3 was also clearly observed. The asymmetric and symmetric N-H-stretching modes  $(3400-3150 \text{ cm}^{-1})$  observed are split due to adsorption on two different Lewis acid sites on the TiO<sub>2</sub> surface [16,31]. Neither of the NH<sub>3</sub>-bending modes was clearly resolved due to overlap with strong nitrate bands in these regions. On the mixed support evidence for the presence of NH<sub>3</sub> was also observed, although the intensity of these bands was somewhat reduced compared to Pd/TiO<sub>2</sub>. In contrast, no evidence for the presence of NH<sub>3</sub> was observed with the Pd/Al<sub>2</sub>O<sub>3</sub> catalyst under these conditions.

# 3.3. The influence of carbon monoxide: NO reduction by $H_2 + CO$

Fig. 9 shows the influence of CO on the H<sub>2</sub>/NO/O<sub>2</sub> reaction over Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/TiO<sub>2</sub> and the Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts, maintaining the total reductant concentration at 4000 ppm (3500 ppm H<sub>2</sub> + 500 ppm CO + 500 ppm NO + 5% O<sub>2</sub>). It is important to note that CO alone is a very poor reductant for NO<sub>x</sub> under these conditions [8]. In the case of Pd/Al<sub>2</sub>O<sub>3</sub>, the presence of a small quantity of CO increased significantly the maximum NO<sub>x</sub> conversion compared to the results obtained with H<sub>2</sub> alone (cf. Fig. 6) from approximately of 6 to ~25%. This increase in NO<sub>x</sub> conversion occurred in the temperature region where reduc-



Fig. 9. Influence of CO on the H<sub>2</sub>/NO/O<sub>2</sub> reaction. Conversion profiles for (a) hydrogen, (b) CO, and (c) NO<sub>x</sub> as a function of temperature over various palladium-containing catalysts. [H<sub>2</sub>] = 3500 ppm, [CO] = 500 ppm, [NO] = 500 ppm, [O<sub>2</sub>] = 5%,  $w/f = 0.03 \text{ g s ml}^{-1}$ .



Fig. 10. Influence of  $[H_2]/([H_2] + [CO])$  ratio on total NO reduction and corresponding nitrogen selectivity in the temperature range 130–170 °C for Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. Total reductant concentration maintained at 4000 ppm. [NO] = 500 ppm,  $[O_2] = 5\%$ , w/f = 0.03 g s ml<sup>-1</sup>.

tant conversion approaches 100% (the oxidation of CO and H<sub>2</sub> track each other closely with all three catalysts). In the case of the Pd/TiO<sub>2</sub> catalyst this improvement in catalytic performance on addition of CO did not occur. In fact the presence of CO actually decreased the  $NO_x$  conversion compared to the values obtained in its absence, as shown by comparison with Fig. 6. The low-temperature reduction feature was shifted by 20 °C toward higher temperature and the maximum NO<sub>x</sub> conversion decreased from  $\sim$  70% to less than 40%. However, the high-temperature process was not directly influenced by the presence of CO (additional experiments showed that the level of  $NO_x$  conversion obtained via this mechanism is influenced only by the absolute  $H_2$ concentration and not the H2:CO ratio). For the mixed support Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> sample, as with Pd/Al<sub>2</sub>O<sub>3</sub>, a beneficial effect was again observed on addition of CO. However, in this case the promotional influence of CO was even greater than that observed with Pd/Al<sub>2</sub>O<sub>3</sub>, with 100% NO<sub>x</sub> conversion being obtained over the temperature range 135–155 °C under these conditions. Of the various TiO<sub>2</sub> loadings tested (2.5, 10, and 25 wt% TiO<sub>2</sub>), the 10 wt% TiO<sub>2</sub> sample was

found to display the best performance, presumably due to its containing the optimum balance between  $TiO_2$  and  $Al_2O_3$  sites, as is discussed in more detail below.

The influence of the H<sub>2</sub>:CO ratio on  $NO_x$  conversion at four different temperatures over Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> is shown in Fig. 10. In these experiments the catalyst was maintained at the specified temperature while the ratio of H<sub>2</sub>:CO was varied. The total reductant concentration in all cases was maintained at 4000 ppm. The corresponding nitrogen selectivity, defined as  $%S_{N_2} = [N_2]/([N_2] +$  $[N_2O]$  × 100, is also shown. Very high NO<sub>x</sub> conversions were achieved over a relatively wide range of H<sub>2</sub>:CO ratios. In general, increasing the CO concentration results in an increase in the temperatures at which the highest  $NO_x$ conversions were observed. This reflects the shift in reductant light-off temperatures that occurs.  $NO_x$  conversions > 80% were achieved with  $[H_2]/([H_2] + [CO])$  values in the range 0.5-0.9 and temperatures of 150-180°C. The nitrogen selectivity increased with increasing temperature and displayed a slight tendency to decrease with increasing CO concentration. Under conditions delivering complete  $NO_x$ conversion, nitrogen selectivities in the range 65-85% were observed.

The corresponding DRIFT spectra obtained at  $150 \,^{\circ}$ C from Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/TiO<sub>2</sub>, and Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, in the presence of H<sub>2</sub> + CO + NO + O<sub>2</sub> (3000 ppm H<sub>2</sub> + 1000 ppm CO + 500 ppm NO + 5% O<sub>2</sub>) are shown in Fig. 11. Most of the bands observed below 1700 cm<sup>-1</sup> are assigned to various nitrate/nitrite, carbonate, and bicarbonate species as discussed in detail elsewhere [9]. Evidence for the presence of NH<sub>3</sub> species was obtained on both Al<sub>2</sub>O<sub>3</sub>-containing catalysts (i.e., those which show improved performance in the



Fig. 11. In situ DRIFT spectra obtained with various supported palladium catalysts in flowing  $H_2 + CO + NO + O_2$  at 150 °C. [H<sub>2</sub>] = 3000 ppm, [CO] = 1000 ppm, [NO] = 500 ppm, [O<sub>2</sub>] = 5%.

presence of CO). On Pd/Al<sub>2</sub>O<sub>3</sub> the band at 1609 cm<sup>-1</sup> is assigned to a bending mode of adsorbed NH<sub>3</sub>. This assignment is in agreement with the appearance of a broad feature at  $\sim$  3250 cm<sup>-1</sup> characteristic of N–H-stretching vibrations. On Pd/TiO\_2/Al\_2O\_3 the 1609  $\mbox{cm}^{-1}$  mode was obscured due to the presence of strongly absorbing nitrate bound to TiO<sub>2</sub> sites. However the N-H-stretching modes (3246 and  $3193 \text{ cm}^{-1}$ ) were much more prominent with this catalyst, indicating a higher NH<sub>3</sub> concentration and accounting for the much-improved activity of Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. No evidence was obtained for the presence of  $NH_x$  species on the Pd/TiO<sub>2</sub> sample at this temperature. Bands in the  $2100-1900 \text{ cm}^{-1}$ region are assigned to various adsorbed CO species as discussed below. Formate was also observed on the Pd/Al2O3 catalyst (3005, 2910, and 1592  $\text{cm}^{-1}$ ), although this species has been shown to be a spectator under the conditions employed [9].

It should be noted that in the absence of CO no evidence for the presence of NH<sub>3</sub> species was obtained on either Pd/Al<sub>2</sub>O<sub>3</sub> or Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> at this temperature (150 °C). This is illustrated in Fig. 12 for the Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. The N–H- and O–H-stretching frequency regions of spectra obtained in the presence of two different gas-phase compositions are shown. In the presence of 4000 ppm H<sub>2</sub> + 500 ppm NO + 5% O<sub>2</sub> (spectrum **A**) a broad feature was observed with a maximum ~ 3400 cm<sup>-1</sup>, which is characteristic of hydrogen bonded O–H groups. On replacing part of the H<sub>2</sub> feed by CO (3000 ppm H<sub>2</sub> + 1000 ppm CO + 500 ppm NO + 5% O<sub>2</sub>, spectrum **B**), weak new features characteristic of N–H-stretching modes developed in the 3300–3100 cm<sup>-1</sup> region. The insert shows the corresponding difference spectrum, which accentuates the N–H-



Fig. 12. In situ DRIFT spectra showing influence of CO on the intensity of N–H-stretching modes at 150 °C over Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>. Spectrum **A**:  $[H_2] = 4000$  ppm, [NO] = 500 ppm,  $[O_2] = 5\%$ . Spectrum **B**:  $[H_2] = 3000$  ppm, [CO] = 1000 ppm, [NO] = 500 ppm,  $[O_2] = 5\%$ . Inset shows corresponding difference spectrum.

stretching modes at 3251 and 3180 cm<sup>-1</sup>. The negative band at 3708 cm<sup>-1</sup> is attributable to loss of "free" O–H groups due to their hydrogen bonding with adsorbed NH<sub>3</sub> [16]. The shoulder at 2821 cm<sup>-1</sup> is consistent with the presence of NH<sub>4</sub><sup>+</sup> species also [32].

The most likely route for NH3 formation requiring participation of CO is via the generation and subsequent hydrolysis of NCO species. However, NCO was never observed in DRIFT spectra when H<sub>2</sub> was present in the gas feed, most likely due to its very rapid hydrolysis under these conditions. We have previously shown that while NCO preformed on a  $Pd/Al_2O_3$  catalyst was relatively stable in flowing NO +  $O_2$ , it was rapidly consumed in a flow containing  $H_2 + NO + O_2$ yielding NH<sub>3</sub> and CO<sub>2</sub> [9]. That NCO is indeed produced on our Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst in the absence of H<sub>2</sub> is shown by the results presented in Fig. 13. Here the spectra obtained from Pd/TiO<sub>2</sub>, Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts after 1 h in a flow containing 4000 ppm CO + 500 ppm NO + 5% O<sub>2</sub> at 150 °C are compared. The corresponding time-resolved spectra in the region  $2300-1700 \text{ cm}^{-1}$  are shown in Figs. 14, 15, and 16 for Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, and Pd/TiO<sub>2</sub>, respectively.

On Pd/Al<sub>2</sub>O<sub>3</sub> bands were observed at 2152 and 2080 cm<sup>-1</sup> assigned to linear Pd<sup>+</sup>–CO and Pd<sup>0</sup>–CO, respectively [33–35]. Bridging and triply bonded carbonyl species were also observed, as shown by the bands at 1975 and 1911 cm<sup>-1</sup> [33,35]. The bands at 2255 and 2233 cm<sup>-1</sup> may be assigned with confidence to isocyanate (NCO) species adsorbed on the alumina support [36–38]. The appearance of two bands could be due to either adsorption of isocyanate on two different surface sites [37,39], or to the presence of covalently bonded NCO and anionic NCO<sup>-</sup> [40]. All the bands



Fig. 13. In situ DRIFT spectra obtained with various supported palladium catalysts in flowing CO + NO + O<sub>2</sub> at 150 °C. [CO] = 4000 ppm, [NO] = 500 ppm, [O<sub>2</sub>] = 5%.



Fig. 14. Time-resolved DRIFT spectra showing accumulation of surface species following introduction of CO + NO + O<sub>2</sub> flow to the DRIFTS cell containing a Pd/Al<sub>2</sub>O<sub>3</sub> sample at 150 °C. [CO] = 4000 ppm, [NO] = 500 ppm, [O<sub>2</sub>] = 5%.



Fig. 15. Time-resolved DRIFT spectra showing accumulation of surface species following introduction of  $CO + NO + O_2$  flow to the DRIFTS cell containing a Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> sample at 150 °C. [CO] = 4000 ppm, [NO] = 500 ppm, [O<sub>2</sub>] = 5%.

below  $1650 \text{ cm}^{-1}$  can once again be assigned to various nitrate/nitrite and carbonate/bicarbonate species [9,13].

On the Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> sample an intense peak was observed at 1801 cm<sup>-1</sup> assigned to a Pd<sup>+</sup>–NO species [22,23], with a shoulder at 1730 cm<sup>-1</sup> indicating the presence of Pd<sup>0</sup>–NO species [22–24]. Alumina-bound NCO (2255/2233 cm<sup>-1</sup>) was also observed on this catalyst. In the 2200–2000 cm<sup>-1</sup> range, in addition to the linear Pd<sup>+</sup>–CO (2150 cm<sup>-1</sup>) and Pd<sup>0</sup>–CO (2084 cm<sup>-1</sup>) observed with Pd/Al<sub>2</sub>O<sub>3</sub>, further bands were observed at 2166 and 2122 cm<sup>-1</sup>. The development of these bands is more clearly seen by referring to the time resolved data in Figs. 14 and 15. On both Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts the Pd<sup>+</sup>–CO and Pd<sup>0</sup>–CO (~2152 and 2080 cm<sup>-1</sup>, respectively) species appeared first, their intensities remaining rela-



Fig. 16. Time-resolved DRIFT spectra showing accumulation of surface species following introduction of CO + NO + O<sub>2</sub> flow to the DRIFTS cell containing a Pd/TiO<sub>2</sub> sample at 150 °C. [CO] = 4000 ppm, [NO] = 500 ppm, [O<sub>2</sub>] = 5%.

tively constant throughout the remainder of the experiment. Within the first few minutes an additional band developed at 2166 cm<sup>-1</sup> on the Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst: *this was not observed with* Pd/Al<sub>2</sub>O<sub>3</sub>. As discussed below, this is assigned to a Pd–NCO species. Although the features in this region were not well resolved on the Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, at least one further species was present, as shown by the gradual increase in intensity in the 2122 cm<sup>-1</sup> region (Fig. 15). This may be due to the generation of cyanide (CN) species [44].

The corresponding time-resolved DRIFT spectra obtained in a flow containing 4000 ppm CO + 500 ppm NO + 5% O<sub>2</sub> over the Pd/TiO<sub>2</sub> sample at 150 °C are shown in Fig. 16. A sharp and intense doublet at  $2168/2159 \text{ cm}^{-1}$  was seen to develop rapidly following introduction of the CO +  $NO + O_2$  reactant mix. This peak is characteristic of NCO adsorbed on the palladium component [41-43]. Interestingly no support-bound NCO was observed on this catalyst in the presence of oxygen, indicating that Ti-NCO species were not stable under these conditions. In separate experiments employing NO + CO only, Ti–NCO species were observed. This is in agreement with the work of Kondarides et al., who investigated the NO + CO +  $O_2$  reaction on Rh/TiO<sub>2</sub>based catalysts and also only observed Ti-NCO species in the absence of gas-phase oxygen [44]. It has also been shown that NCO is considerably less stable on TiO<sub>2</sub> than other supports such as SiO<sub>2</sub> [39]. The intensity of the Pd-NCO feature passed through an initial maximum and then continued to increase gradually throughout the remainder of the experiment. The other prominent feature in this figure is associated with Pd nitrosyl species, Pd<sup>+</sup>-NO at 1974 cm<sup>-1</sup> and  $Pd^0$ –NO at 1735 cm<sup>-1</sup>. The intensity of these features increased rapidly to reach a maximum after  $\sim 10$  min and then decreased gradually thereafter. Similar features were observed on the Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst, Fig. 15, and seem to be associated with the Pd/TiO<sub>2</sub> component. In contrast to the Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> samples, various carbonyl species (2150–1900 cm<sup>-1</sup>) were only observed for a very brief initial period following introduction of the CO + NO + O<sub>2</sub> reactant mix over Pd/TiO<sub>2</sub>.

## 4. Discussion

The key issue is this-why is the mixed support catalyst (Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>) far superior to both Pd/TiO<sub>2</sub> and Pd/Al<sub>2</sub>O<sub>3</sub>? The answer does not reside in formation of mixed or doped oxide phases because the spectroscopic, microscopic, and diffraction data indicate that no such phases are formed. Therefore before discussing the catalytic results it is useful to review briefly structural aspects of the TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mixed support. A similar method to that employed here was used by Schmal and co-workers to prepare a series of **Pt**/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts [45,46]. These materials were characterised by a combination of XRD, TPR, DRS-UV-vis, and TEM and it was concluded that they consisted of a two-dimensional layer of titanium oxide covering the  $\gamma$ -alumina support. This interpretation is consistent with our XRD, XPS, and EDX spectroscopy results for the 10 wt% TiO<sub>2</sub> sample. These suggest that a significant proportion of the titania was present in a very highly dispersed form on the alumina support. XPS gave a Ti:Al surface atomic ratio of 1:3 for this sample. Given the surface area of our Al<sub>2</sub>O<sub>3</sub> starting material (120  $m^2 g^{-1}$ ), a straightforward calculation suggests that monolayer coverage would correspond to approximately 7.0 wt% TiO<sub>2</sub> loading. This is in accord with the HREM results which show that small (2–5 nm) 3D TiO<sub>2</sub> crystallites are also present at 10 wt% TiO<sub>2</sub> loading. However, note that complete coverage of the alumina was not achieved with this titania loading, as shown by TPD/DRIFTS of adsorbed NO<sub>x</sub> species: these data clearly reveal that surface sites associated with the Al<sub>2</sub>O<sub>3</sub> component were still available for adsorption.

The vastly superior performance of Pd/TiO<sub>2</sub> compared to  $Pd/Al_2O_3$  for NO<sub>x</sub> reduction by H<sub>2</sub> (Fig. 6) under oxygenrich conditions has been reported previously [11-13]. We showed that the low-temperature reduction channel found with Pd/TiO<sub>2</sub> (occurring in the temperature range close to H<sub>2</sub> light off) was associated with the formation of reduced palladium (Pd<sup>0</sup>) sites on the catalyst surface [13]. The hightemperature (240 °C) NO<sub>x</sub> reduction channel observed with Pd/TiO2 was shown to occur via the formation and subsequent reaction of ammonia [13]. The strikingly low activity of Pd/Al2O3 under these conditions was due to palladium remaining predominantly in an oxidised state on this support. Why palladium is more easily reduced on TiO<sub>2</sub> as compared to  $Al_2O_3$  is not entirely clear. A possible explanation is that PdO is stabilised on alumina by a strong support interaction, perhaps involving formation of a palladium aluminate phase [47].

In the case of the Pd/10 wt% TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mixed support catalyst, the titania caused a significant increase in NO<sub>x</sub> conversion during the H<sub>2</sub> + NO + O<sub>2</sub> reaction (Fig. 6), resulting in performance similar to Pd/TiO<sub>2</sub>. DRIFTS data clearly revealed that this improvement in performance, in both low- and high-temperature regimes, is attributable to the same mechanisms that occur with Pd/TiO<sub>2</sub>, i.e., formation of reduced Pd and NH<sub>3</sub> species at the relevant temperatures (Figs. 7 and 8). This is good evidence for the close association of Pd and TiO<sub>2</sub> in the mixed support catalyst.

Given the high activity of Pd/TiO<sub>2</sub> for NO<sub>x</sub> reduction by hydrogen, it is of considerable interest to elucidate the response of this catalyst to addition of CO to the  $H_2 + NO + O_2$ gas feed (in real engine exhausts the H<sub>2</sub> and CO concentrations are closely linked due to the water gas-shift reaction). As shown by comparing the results in Figs. 6 and 9, changing the reductant feed from 4000 ppm  $H_2$  to 3500 ppm  $H_2$  + 500 ppm CO resulted in a considerable decrease in the  $NO_x$ conversion achieved via the low-temperature mechanism, involving dissociation of NO on reduced metal sites, over this catalyst. Carbon monoxide induced a similar poisoning influence on the  $H_2 + NO + O_2$  reaction over platinum/Al<sub>2</sub>O<sub>3</sub> catalysts [8,48]. This poisoning influence of CO on Pd/TiO2 and Pt/Al<sub>2</sub>O<sub>3</sub> is related to the fact that NH<sub>3</sub> was not formed on these catalysts under reaction conditions, in contrast to the significantly more active Pd/Al<sub>2</sub>O<sub>3</sub> sample. In the absence of NH<sub>3</sub> generation the up-shift in light-off temperature that occurs on addition of CO favours direct combustion of the reductants by  $O_2$  rather than reaction with NO.

In striking contrast to Pd/TiO<sub>2</sub>, the Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> mixed support catalyst exhibited very strong promotion by CO for NO<sub>x</sub> reduction—even more pronounced than in the case of Pd/Al<sub>2</sub>O<sub>3</sub>. The DRIFT spectra in Fig. 11 indicate that this higher activity of Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> compared to Pd/Al<sub>2</sub>O<sub>3</sub> is due to the higher concentration of NH<sub>3</sub> generated on the surface of the former.

Since NH<sub>3</sub> is *not* formed on Pd/TiO<sub>2</sub> in the presence of  $H_2 + CO + NO + O_2$ , how do we account for the fact that the presence of TiO<sub>2</sub> promotes the formation of this species on the mixed support catalyst? To answer this it is necessary to consider the intermediate NCO species. NCO is not observed in the presence of  $H_2 + O_2$  due to its rapid hydrolysis [9]. Therefore to investigate formation of this species it was necessary to remove H<sub>2</sub> from the gas feed. As shown in Fig. 13, in the presence of  $CO + NO + O_2$ , Pd–NCO species are observed in the DRIFT spectra obtained from both Pd/TiO<sub>2</sub> and Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, although the concentration is much greater on the former. Although Pd-NCO is not observed in the DRIFT spectra obtained from Pd/Al<sub>2</sub>O<sub>3</sub>, its presence may be inferred from the observed accumulation of Al-NCO. That is, the NCO species originate on the metal component followed by spillover onto the alumina surface.

What is very clear is that the  $TiO_2$  component of Pd/ $TiO_2$ / Al<sub>2</sub>O<sub>3</sub> catalysts promotes formation of NCO on the surface of metal particles with which it is in intimate contact. It is likely that this translates into enhanced rates of NH<sub>3</sub> forma-

tion when H<sub>2</sub> is added to the gas mix. However, the fact that NH<sub>3</sub> was only observed on Pd/Al<sub>2</sub>O<sub>3</sub> and Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> on addition of H<sub>2</sub>, even though Pd/TiO<sub>2</sub> had the highest concentration of Pd-NCO species in the absence of hydrogen, suggests that the Al<sub>2</sub>O<sub>3</sub> component is necessary for rapid hydrolysis of NCO to ammonia under these conditions. Although both Al<sub>2</sub>O<sub>3</sub> and TiO<sub>2</sub> have been shown previously to be active for NCO hydrolysis [49,50], no direct comparison of the activity of these two oxides for this reaction has been performed. Furthermore, in separate experiments we have observed that NCO species preadsorbed on the support component of Pd/TiO<sub>2</sub> catalysts during the CO + NO reaction were subsequently rapidly consumed when oxygen was added to the gas mix. This accounts for the fact that Ti-NCO species were never observed under the oxygen-rich conditions discussed in this work. In contrast, on Al2O3 preadsorbed NCO was relatively stable in the presence of oxygen but was consumed rapidly in the presence of  $H_2 + O_2$  [9]. Therefore in the presence of the full reaction mix  $(H_2 + CO + NO + O_2)$ , NCO hydrolysis to ammonia dominates on the alumina surface while on TiO<sub>2</sub> rapid NCO combustion may compete with hydrolysis.

How are we to rationalise the observation that TiO<sub>2</sub> promotes the formation of Pd-NCO species? The most likely explanation is in terms of the relative surface coverages of CO and NO on palladium particles supported on the TiO<sub>2</sub> and Al<sub>2</sub>O<sub>3</sub> components, under conditions of competitive adsorption. (Other things being equal, one expects CO to adsorb more strongly than NO.) One of the major differences between the spectra observed with  $Pd/TiO_2$ , Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, and Pd/Al<sub>2</sub>O<sub>3</sub> catalysts in the presence of  $CO + NO + O_2$  is the very different concentrations of Pd carbonyl and Pd nitrosyl species (Figs. 13-16). With Pd/TiO<sub>2</sub> and Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts the surface of the Pd particles is dominated by Pd-NO species (Pd<sup>+</sup>-NO and  $Pd^0$ -NO at 1801/1974 and 1935 cm<sup>-1</sup>, respectively), while on Pd/Al<sub>2</sub>O<sub>3</sub> only carbonyl species (Pd<sup>+</sup>-CO, Pd<sup>0</sup>-CO, and bridged CO at 2152, 2080, and 1975  $\text{cm}^{-1}$ , respectively) are observed. This difference in relative coverage must influence the rate at which NCO is formed, with higher NO concentrations favouring isocyanate production.

The mechanism whereby  $TiO_2$  affects Pd particles so as to strongly favour NO adsorption may be purely electronic in origin. However, it also possible that  $TiO_2$  is directly involved in the catalytic reaction. Reducible metal oxides such as CeO<sub>2</sub> are known to participate in CO oxidation by reacting with CO molecules adsorbed near the metal-support interface, generating CO<sub>2</sub> and oxygen vacancies [51]. In the present case this process could result in a reduction of the steady-state CO coverage on the Pd surface, thus enhancing the NO coverage.

Although our results strongly suggest that NCO species are intermediates in the enhanced conversion of NO in the presence of  $H_2$  + CO over Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, the role of  $H_2$ cannot solely be that of generating H<sub>2</sub>O for subsequent NCO hydrolysis. This was demonstrated by the result of control experiments in which H<sub>2</sub> was replaced by H<sub>2</sub>O, where it was found that the promoting effect of directly added water was substantially less than that of hydrogen. Factors contributing to this clear difference between the effects of hydrogen and water could be as follows. NCO formation on the metal surface occurs via reaction between adsorbed CO and N. Formation of the latter, by NO dissociation, is likely to be the rate-determining step [52]. It is significant, therefore, that enhanced rates of NO dissociation have been observed in the presence of hydrogen [53-55]. Note also that the intense Pd–NO bands at 1800 and 1735  $cm^{-1}$  we observed in the presence of  $CO + NO + O_2$  on Pd/TiO<sub>2</sub> and Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (Fig. 13) were not seen in the presence of  $H_2 + CO + NO + O_2$  (Fig. 11), consistent with extensive NO dissociation in the later case. Moreover, the bands due to the linear and bridged Pd-CO species observed on Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> in the presence of  $CO + NO + O_2$ (Fig. 13, 2084 and 1974 cm<sup>-1</sup>, respectively) were significantly red-shifted in the presence of hydrogen (to 2064 and 1956 cm<sup>-1</sup>, respectively; Fig. 11). This is attributed to coadsorbed hydrogen weakening the C-O bond by enhancing back-donation of electron density into the CO antibonding  $\pi$  orbital [56,57]. The same would be expected with NO, weakening the N-O bond and thus enhancing the rates of NO dissociation in the presence of  $H_2$  [53–55]. This in turn would increase the rate of NCO production and subsequent NH<sub>3</sub> formation.

An alternative explanation for the role of hydrogen in this system relates to the mobility of isocyanate species. Lorimer and Bell [58] found while investigating the CO + NO reaction over a Pt/SiO<sub>2</sub> disk that NCO species were deposited on a second SiO<sub>2</sub> disk located centimeters away in the same in situ infrared cell. This was explainable only via the generation of gas-phase HNCO, with the source of hydrogen considered to be reverse spillover of hydroxyl groups from the support to the metal surface. In the present case it is possible therefore that the role of hydrogen is to enhance the rate of migration of isocyanate species from the metal to the support via the generation of gas-phase HNCO.

Although the Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst discussed here delivers extremely high  $NO_x$  conversions under demanding conditions, which includes the presence of additional water vapour [14], there remain aspects of this system that could be significantly improved. It is clear from Fig. 10 that the highest  $NO_x$  conversions are achieved with relatively H<sub>2</sub>-rich mixtures. Although > 80% NO<sub>x</sub> conversion can be achieved at the 1:3 H<sub>2</sub>:CO ratio encountered in most engine exhausts, improving the performance of the system under more CO-rich conditions would clearly be desirable. Widening the temperature range over which the catalyst maintains very high  $NO_x$  conversions would also be beneficial, although the fact that NH<sub>3</sub> is also formed via a second, high-temperature mechanism ensures that the significant NO<sub>x</sub> conversion (> 50%) can be maintained over a very wide temperature range (150 °C in the data shown in Fig. 9). Identifying suitable promoters could be one method of achieving these aims. Overall, we believe this system represents a promising alternative strategy for the control of  $NO_x$  emissions generated under oxygen-rich conditions.

#### 5. Conclusions

- 1. Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts provide very high (100%) NO<sub>x</sub> conversions under demanding conditions (low temperature, high oxygen excess) in the presence of mixed  $H_2$  + CO reductant feeds. A second high-temperature NO<sub>x</sub> reduction channel also operates which greatly extends the useful temperature range.
- 2. Both NO<sub>x</sub> reduction channels generate NH<sub>3</sub> in situ. The low-temperature channel operates via formation and subsequent hydrolysis of NCO species while the high-temperature channel forms NH<sub>3</sub> directly from reaction between H<sub>2</sub> and NO.
- 3. The observed synergy between titania and alumina derives from the intrinsic surface chemistry of the pure oxides and not from mixed oxide formation. Thus the Pd/TiO<sub>2</sub> component of the Pd/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst is active toward NCO production while the Al<sub>2</sub>O<sub>3</sub> component promotes subsequent hydrolysis of NCO to ammonia.

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