The positive effect of hydrogen on the reaction of nitric oxide with carbon monoxide over platinum and rhodium catalysts

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The effect of adding 330–4930 ppm hydrogen to a reaction mixture of NO and CO (2000 ppm each) over platinum and rhodium catalysts has been investigated at temperatures around 200–250°C. Hydrogen causes large increases in the conversion of NO and, surprisingly, also of CO. Oxygen atoms from the additional NO converted are eventually combined with CO to give CO_2 rather than react with hydrogen to form water. This reaction is described by $CO + NO + \frac{3}{2}H_2 \rightarrow CO_2 + NH_3$ and accounts for 50–100% of the CO_2 formed with Pt/Al_2O_3 and 20–50% with Rh/Al_2O_3. With the latter catalyst a substantial amount of NO converted produces nitrous oxide. Comparison with a known study of unsupported noble metals suggests that isocyanic acid (HNCO) might be an important intermediate in a reaction system with NO, CO and H_2 present.

Keywords: nitric oxide; carbon monoxide; hydrogen; Pt/Al_2O_3; Rh/Al_2O_3

1. Introduction

Vehicle exhaust gases are complex mixtures, the composition of which depends on engine operating conditions [1]. Catalytic converters are used to minimise pollutants in the gas stream, mainly by reducing nitrogen oxides to nitrogen and by oxidising carbon monoxide, unburnt hydrocarbons and hydrogen [1–3]. There is considerable interest in understanding and optimising the reactions occurring in the converters [4].

Studies have been focused on catalyst performance using actual exhaust gases

[5,6] or simulated mixtures [7–9]. Individual reactions over one or more supported precious metal exhaust catalysts have been examined. Thus, for example, the rate of NO reduction over supported Pt increases in the order [10–15] $NO + H_2 > NO + CO + H_2 > NO + CO$. This behaviour is generally attributed to inhibition of NO dissociation by strong CO adsorption [12–14,16]. A similar pattern is observed over supported Rh [13], with differences being smaller.

In a previous study [17] we examined the behaviour of the three-component systems, $NO + CO + H_2$ and $NO + CO + H_2O$, over alumina supported Pt and Rh. The inclusion of hydrogen led to a substantial increase in the conversion of NO, and more surprisingly, of CO as well. With Pt/Al_2O_3 the nitrogen atom from the additional NO converted formed largely ammonia while the oxygen atom reacted to give CO_2 rather than water.

The present studies are intended to explore in more detail these preliminary findings, using the reaction between NO and CO in the presence of hydrogen as a test example.

2. Experimental

The catalytic experiments were performed in a continuous flow tubular reactor (Pyrex, 8 mm o.d., 5 mm i.d.) with the catalyst held between two plugs of quartz wool on top of a thermocouple. The gas mixture was made up from four streams (UHP helium and three analysed mixtures also in UHP helium) supplied by separate calibrated mass flow controllers.

Product and feed analyses were performed on-line by infrared spectroscopy (IR) and mass spectrometry (MS). The former method used a dispersive infrared spectrometer (Perkin-Elmer 580B) with a multiple pass cell (2.4 m total path length) and a control computer. A routine was developed by which the absorbances of CO (2117 cm^{-1}), NO (1877 cm^{-1}), N_2O (1300 cm^{-1}), NH_3 (965 cm^{-1}) and CO_2 (679 cm^{-1}) were repeatedly acquired and stored on a cycle time of approximately 7 min. A quadrupole mass spectrometer (Vacuum Generators model 300SX) was used to quantify H_2 ($m/z = 2$), CO ($m/z = 12$), CO_2 ($m/z = 22$) and NO ($m/z = 30$). Further details are given elsewhere [17].

The Pt/Al_2O_3 and Rh/Al_2O_3 catalysts were prepared by incipient wetness of powdered Al_2O_3 (Condea washcoat grade, surface area $\approx$ 140 m^2/g) with sufficient aqueous H_2PtCl_6 or $RhCl_3$ solution to yield nominal metal contents of 1 wt% Pt and 0.53 wt% Rh respectively. The slurries were dried at 50°C under mild vacuum in a rotary evaporator, then at 100°C overnight with subsequent calcination for 4 h at 500°C. The resulting powders were pressed, crushed and sieved to give a 106–180 μm fraction. The platinum and rhodium dispersions were 64 and 28% respectively as measured after the activity tests by the adsorption of CO at room temperature using a pulse adsorption technique and assuming one CO molecule per metal atom. The Pt/SiO_2 catalyst was number 40-SiO_2-PtCl-L in the series prepared and characterised by Burwell et al. [18]. It was made by impregnation of Davison grade 62 silica (285 m^2/g) and contained 1.10 wt% Pt with a dispersion (measured by H_2 chemisorption) of 40%. The catalysts were pretreated in a temperature programmed reduction (1% H_2/He, 9°C/min up to 500°C) followed by a 30 min equilibration with 2000 ppm of CO and NO at 500°C and slow cooling in the same mixture to reaction temperature. In case of Pt/SiO_2 the maximum temperature during pretreatment was 350°C.

The catalytic experiments were carried out using 75 mg samples of each catalyst and with a total flow rate of 100 ml/min (STP) giving a GHSV of $\sim$50 000 h^{-1}. Concentrations of NO and CO were 2000 ppm each in all experiments. In the steady-state isothermal experiments with Pt/Al_2O_3 and Rh/Al_2O_3 the data were obtained by running the operating conditions for at least 21 min (three IR analyses of the five gases) between each change in hydrogen concentration. Hydrogen was introduced with inlet concentrations chosen in random order (0, 890, 2470, 630, 1230, 330, 1640, 4930 and 0 ppm). The effect of hydrogen (0 versus 890 ppm) was also investigated with Pt/SiO_2 and Pt/Al_2O_3 in isothermal experiments and in comparative temperature programmed reaction experiments in which the reaction was commenced at 150°C and ramped to 350°C at 2°C/min. Only the Pt/SiO_2 catalysts yielded similar results in both types of experiments and only these results are considered here.

3. Results

Initial experiments were carried out using a mixture of nitric oxide (2000 ppm) and carbon monoxide (2000 ppm) over a Pt/SiO_2 catalyst in the absence and presence of hydrogen (890 ppm). The reactions were investigated as a function of temperature (figs. 1 and 2).

The effect of hydrogen on the conversions of NO and CO was immediately obvious. The conversion of NO was significantly increased over the temperature range 190–300°C, with hydrogen being fully converted by 230°C (fig. 1).

CO conversion was also increased, although to a lesser extent than NO (fig. 2). Conversion increased sharply above 270°C, suggesting that water, produced from hydrogen, could be responsible for at least part of the increase in CO conversion above that temperature. An enhancement by water at temperatures $\geqslant$270°C was described previously [17].

Silica is not normally used in car exhaust catalysts, and comparisons were then made with alumina supported Pt and Rh. In that hydrogen was not entirely consumed at temperatures less than 230°C, a temperature of 210°C was chosen for detailed study.

The effect of adding various amounts of hydrogen to NO/CO mixtures reacting over Pt/Al_2O_3 at 210°C is shown in figs. 3 and 4. Consumption of hydrogen was complete for addition levels less than 1000 ppm. Both the consumption of NO and,

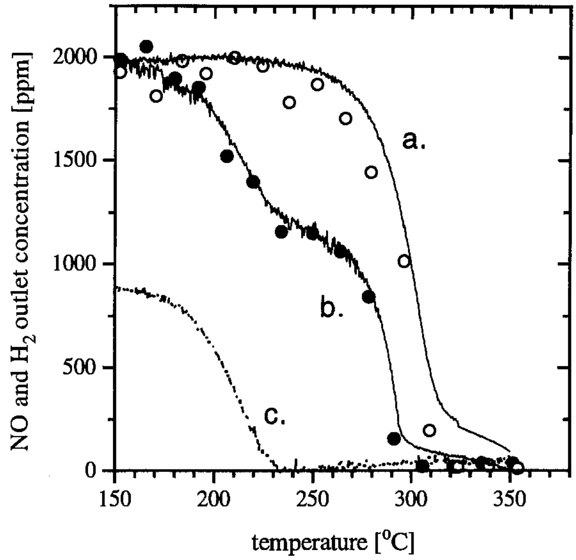

Fig. 1. Effect of 890 ppm of hydrogen on the temperature programmed reaction of 2000 ppm NO and 2000 ppm CO over Pt/SiO_2: (a) outlet NO concentrations during reaction of NO and CO alone, (b) outlet NO concentrations during reaction of NO, CO and H_2, (c) outlet H_2 concentration during (b). In each case the solid lines are the MS measurements and the points the IR determinations.

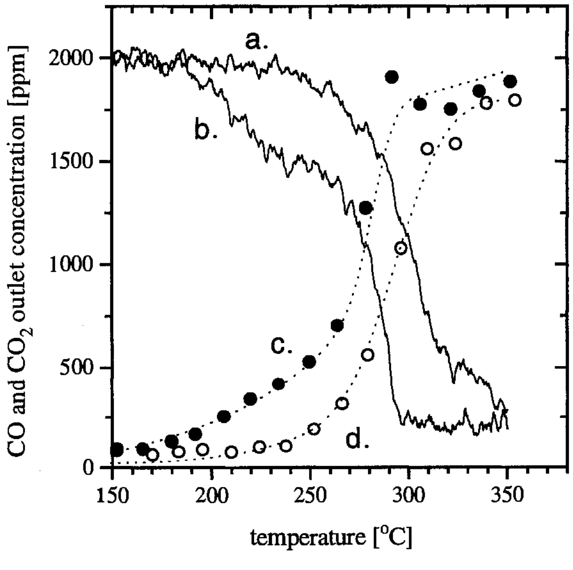

Fig. 2. Outlet CO (a, b by MS) and CO_2 (c, d by IR) concentrations for the experiments of fig. 1: (a, d) reaction of NO and CO alone, (b, c) reaction of NO, CO and H_2.

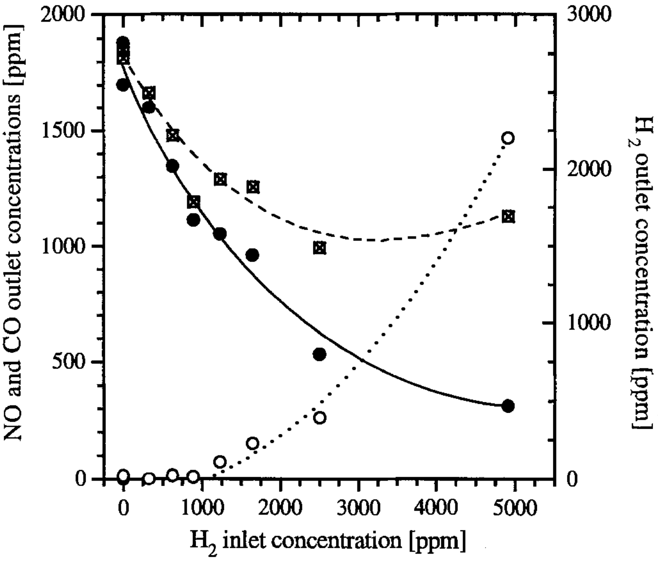

Fig. 3. Effect of hydrogen concentration on the reaction between 2000 ppm NO and 2000 ppm CO over Pt/Al_2O_3 at 210°C; (●) NO (by MS), (☒) CO (by IR), (○) H_2 (by MS).

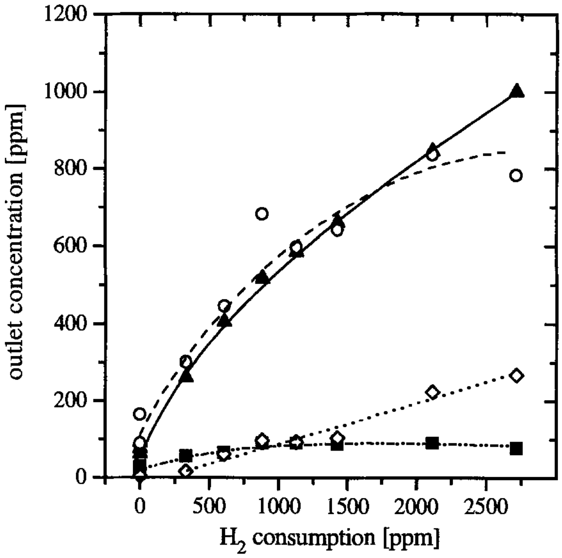

Fig. 4. Product formation during the reaction of 2000 ppm NO and 2000 ppm CO in the presence of hydrogen over Pt/Al_2O_3 at 210°C; (▲) NH_3 (by IR), (○) CO_2 (average of IR and MS values), (■) N_2O (by IR), (◇) N_2 (calculated by mass balance).

surprisingly, of CO was increased by the presence of hydrogen. Thus the increase in NO conversion is not due simply to the superposition of separate reduction processes involving CO and H_2.

The product concentrations plotted against hydrogen consumption (rather than input hydrogen concentrations) are shown in fig. 4. The major products are ammonia and carbon dioxide, formed in similar amounts under all conditions. N_2O and N_2 were always minor products. Thus the oxygen atom of NO becomes incorporated mainly into CO_2 rather than into H_2O, while the nitrogen atom reacts mainly to form ammonia. The selectivity of the oxygen atom towards CO_2 is close to 100% at low hydrogen concentration, see also ref. [17], but decreases to around 35% at the highest concentration of H_2 (4930 ppm), based on the amount of H_2O produced as calculated by hydrogen and oxygen mass balances.

Similar experiments were carried out using Rh/Al_2O_3 (figs. 5 and 6). Conversions of both NO and CO were increased on addition of hydrogen (fig. 5), with more NO being converted than over Pt/Al_2O_3. Hydrogen consumption was never complete.

The product distribution as a function of hydrogen consumption over Rh/Al_2O_3 is shown in fig. 6. Ammonia production was similar to that observed over Pt/Al_2O_3 but the amounts of CO_2 and N_2O produced were much higher. The differences between Pt/Al_2O_3 and Rh/Al_2O_3 are quantified in table 1 for several hydrogen inlet concentrations.

Thus, the selectivity of ammonia production from NO over supported Rh is less than that over supported Pt and a significant fraction of the N atoms are converted to N_2O.

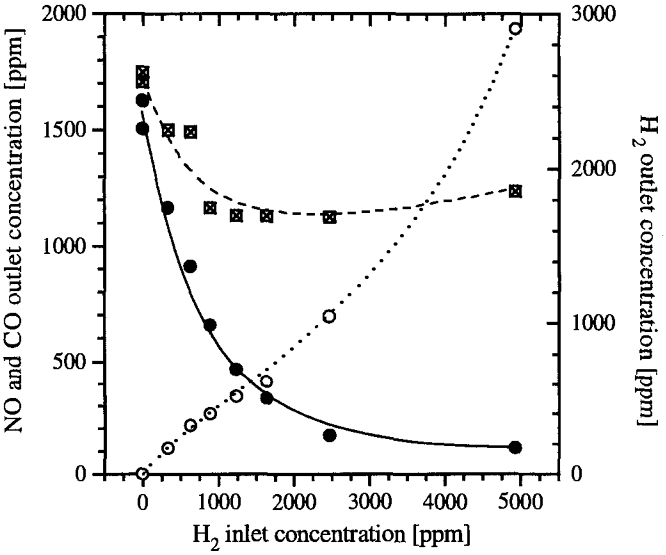

Fig. 5. Effect of hydrogen concentration on the reaction between 2000 ppm NO and 2000 ppm CO over Rh/Al_2O_3 at 210°C: (●) NO (by MS), (☒) CO (by IR), (○) H_2 (by MS).

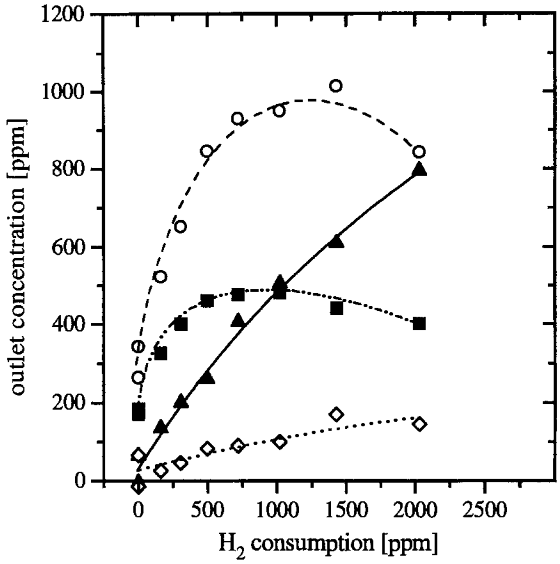

Fig. 6. Product formation during the reaction of 2000 ppm NO and 2000 ppm CO in the presence of hydrogen over Rh/Al_2O_3 at 210°C; (▲) NH_3 (by IR), (○) CO_2 (average of IR and MS values), (■) N_2O (by IR), (◇) N_2 (calculated by mass balance).

4. Discussion

The addition of hydrogen to mixtures of CO and NO reacting over supported Pt and Rh catalysts is found to increase the conversion both of CO and of NO (figs. 1, 2, 3 and 5). In the absence of hydrogen, the expected reactions are

Table 1

Comparison of conversions and selectivities with Pt/Al_2O_3 and Rh/Al_2O_3 for similar hydrogen inlet concentrations and consumption. Concentrations of NO and CO were 2000 ppm each, the catalyst weight was 75 mg and the total flow rate 100 ml/min (STP)

Catalyst	H_2 (ppm)		Conversion (%)			Selectivities of underlined atoms to (%)			
	inlet	consumed	H_2	NO	CO	$N\underline{H}_3$ [a]	$C\underline{O}_2$ [b]	$\underline{N}_2O$ [c]	$\underline{N}H_3$ [d]
Pt/Al_2O_3	0	–	–	11	9	–	–	~ 50	–
210°C	1640	1415	86	50	37	70	57	20	62
Rh/Al_2O_3	0	–	–	25	13	–	–	~ 67	–
210°C	1640	1020	62	83	44	74	80	50	27
	2470	1430	58	92	44	64	68	42	30

[a] Selectivity of the hydrogen atom, $H \rightarrow NH_3 = 3NH_3/(H_{2in} - H_{2out})$.

[b] Selectivity of the oxygen atom, $N(O) \rightarrow CO_2 = CO_2/(CO_2 + H_2O)$ with H_2O by H-balance, i.e. $H_2O = H_{2in} - H_{2out} - 1.5NH_3$.

[c] Selectivity of the nitrogen atom, $(N)O \rightarrow N_2O = 2N_2O/(NO_{in} - NO_{out})$.

[d] Selectivity of the nitrogen atom, $N(O) \rightarrow NH_3 = NH_3/(NO_{in} - NO_{out})$.

$$NO + CO \rightarrow \tfrac{1}{2}N_2 + CO_2 \qquad (1)$$

$$NO + \tfrac{1}{2}CO \rightarrow \tfrac{1}{2}N_2O + \tfrac{1}{2}CO_2 \qquad (2)$$

Additional reactions expected on adding hydrogen include

$$NO + \tfrac{5}{2}H_2 \rightarrow NH_3 + H_2O \qquad (3)$$

$$NO + H_2 \rightarrow \tfrac{1}{2}N_2 + H_2O \qquad (4)$$

$$NO + \tfrac{1}{2}H_2 \rightarrow \tfrac{1}{2}N_2O + \tfrac{1}{2}H_2O \qquad (5)$$

None of these reactions necessitate increases in CO conversion, or CO_2 formation, as observed experimentally over all catalysts (figs. 1, 2 and 5). Indeed, in some cases (Pt/Al_2O_3, fig. 4), nearly all of the O atoms from NO were converted to CO_2.

One possibility is that water, produced from hydrogen, reacts with CO via the water–gas shift reaction to produce CO_2,

$$H_2O + CO \rightarrow H_2 + CO_2 \qquad (6)$$

Mixtures of H_2O and CO were passed over alumina supported catalysts at 210°C. The formation of hydrogen was less than 25 ppm, indicating that reaction (6) is unimportant.

A substantial part of the overall reaction must then be presented as

$$CO + NO + \tfrac{3}{2}H_2 \rightarrow CO_2 + NH_3 \qquad (7)$$

It is possible to estimate the importance of reaction (7) over the two catalysts. If it

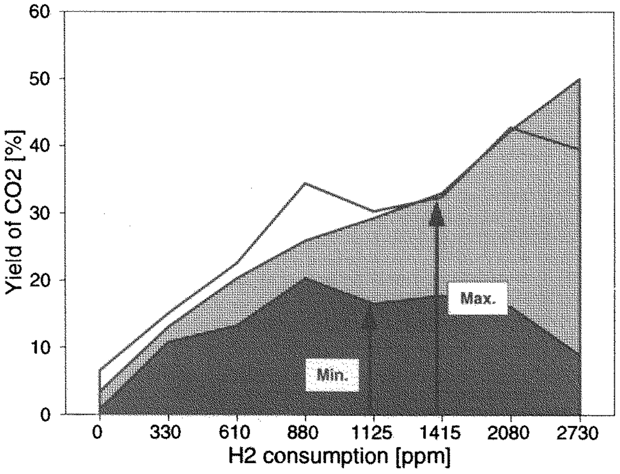

Fig. 7. Measured CO_2 yield (upper line) with Pt/Al_2O_3, as in fig. 4, and the minimal (filled area) and maximal (filled and hatched area) portion attributable to the presence of the net reaction (7): $CO + NO + \tfrac{3}{2}H_2 \rightarrow CO_2 + NH_3$.

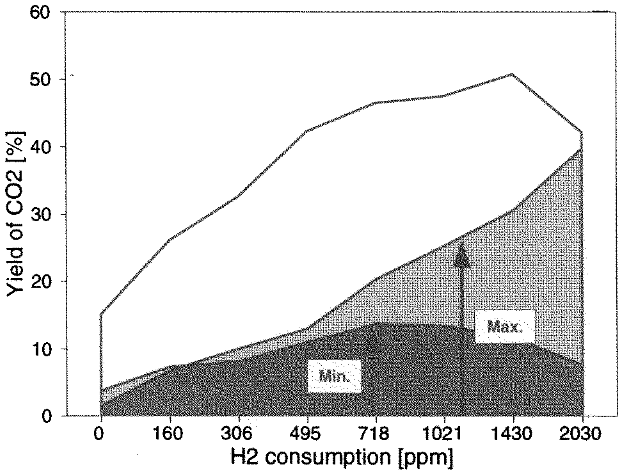

Fig. 8. Measured CO_2 yield with Rh/Al_2O_3, as in fig. 6. Same legend as in fig. 7.

is assumed that all N_2 and N_2O comes via reactions (1) and (2), then this will be associated with the production of corresponding amounts of CO_2. Subtracting this amount (calculated from the yield of N_2 and N_2O) from the observed values gives the minimum yield of CO_2 formed by the net reaction (7).

If, on the other hand, N_2 and N_2O originate only from reactions (4) and (5), then the maximum yield of CO_2 due to reaction (7) is equal to the amount of NH_3 formed. It is accepted that NH_3 could also be produced by reaction (3) but for the maximum case the yield of CO_2 and NH_3 should be equal (reaction (7)). If the CO_2 yield is larger than NH_3, as for rhodium, than this excess of CO_2 must be produced via reactions (1) and (2).

Minimum and maximum yields of CO_2 due to the net reaction (7) are shown in figs. 7 and 8 for Pt/Al_2O_3 and Rh/Al_2O_3 respectively. The net reaction is important over alumina supported catalysts, with 50–100% of the CO_2 being produced via reaction (7) over the Pt/Al_2O_3 catalyst and 20–50% over the Rh/Al_2O_3 catalyst.

These findings can be rationalised by considering possible mechanisms of reaction. It is widely accepted that the first step in the reaction of NO involves the dissociation of adsorbed molecules [19–21],

$$^*NO + * \rightarrow {}^*N + {}^*O \qquad (8)$$

CO also adsorbs on the surface, strongly on Pt [19,22–24] and less strongly on Rh [23,25,26]. The reaction between NO and CO is then suggested to involve reaction between adsorbed O and adsorbed CO together with recombination of adsorbed N atoms or reaction between adsorbed *N and *NO,

$$^*O + {}^*CO \rightarrow CO_2 + 2* \qquad (9)$$

$$^*N + {}^*N \rightarrow N_2 + 2* \qquad (10)$$

$$^*N + {}^*NO \rightarrow N_2O + * \qquad (11)$$

$$^*N + {}^*NO \rightarrow N_2 + {}^*O \qquad (12)$$

These reactions are thought to be inhibited by the strong adsorption of CO on Pt [12,16,23], or of NO on Rh [16,27], under conditions pertinent to this investigation.

Hydrogen is now found to have a striking effect on the rate of NO conversion (table 1) and on the product selectivity. Two possible explanations for these effects may be considered. One involves steps confined to the metal, the other a combination of metal and support processes. As discussed previously [17], adsorbed hydrogen could scavenge the surface of nitrogen atoms, formed from NO by reaction (8), to give ammonia,

$$^*N + 3H^* \rightarrow NH_3 + 4*, \qquad (13)$$

while the oxygen from NO reacts with adsorbed CO, which adsorbs much more strongly than H_2 on Pt [27]. The difficulty is that removal of adsorbed nitrogen would be expected to lead to an increase in NO conversion only if the NO + CO reaction was limited to a significant extent by nitrogen coverage, as well as CO coverage, and this has not been established experimentally. A rate enhancement on a CO dominated surface could be explained via a reaction first suggested by Hecker and Bell [28],

$$^*NO + {}^*H \rightarrow {}^*N + {}^*OH \qquad (14)$$

Shustorovich and Bell [29] calculated that the activation energy for this reaction would be considerably less than that of the corresponding step to give $^*NH + {}^*O$, or of that for simple dissociation, reaction (8). Hirano et al. [30] rejected the possibility of hydrogen assisted dissociation under UHV conditions but, nonetheless, reaction (14) could be more important under conditions of higher coverage. The difficulty with reaction (14) is that it leads to the oxygen from NO being attached to hydrogen and that would be expected to result in the formation of water rather than CO_2 as observed.

The explanation we favour involves a combination of metal and support catalysed processes with NCO groups, formed on Pt as suggested by Solymosi and Kiss [31],

$$^*N + {}^*CO \rightarrow {}^*NCO \qquad (15)$$

as a key intermediate. Subsequent reaction with adsorbed hydrogen could result in the desorption of gaseous isocyanic acid (HNCO),

$$^*NCO + {}^*H \rightarrow HNCO, \qquad (16)$$

readsorption onto the support and reaction with water to produce NH_3 and CO_2,

$$HNCO + H_2O \rightarrow NH_3 + CO_2 \tag{17}$$

Herein, water is a reaction intermediate formed by reactions such as (3), (4) and (5) and consumed by reaction (17). Both formation and hydrolysis of support-bounded isocyanate species are well known reactions [21,32–34].

In this connection, Voorhoeve and Trimble [35,36] have studied the reaction of NO, CO and H_2 over unsupported Pt. The major product was described as ammonium cyanate (NH_4OCN) with very little formation of NH_3. The same product distribution was observed for other unsupported noble metals [35–37], with high selectivity to the cyanate being reported in all cases. The turnover numbers observed were quite similar to those found in the present study (table 2), even though the conditions are somewhat different. The observed NH_4OCN seems an unlikely primary product in the gas phase but may well be formed by reaction of HNCO with NH_3, reaction (18), in the cooler parts of a reactor downstream or during the liquid phase absorption stage of the analytical method they employed [38],

$$HNCO + NH_3 \rightarrow NH_4OCN \tag{18}$$

Formation of HNCO as an intermediate and its subsequent hydrolysis (reactions (16) and (17)) would also fit with the lower extent of formation of NH_3 and CO_2 using Pt/SiO_2 rather than Pt/Al_2O_3 (table 3). The hydrolysis reaction is presumably faster on Al_2O_3 than on SiO_2 and this would explain the higher amounts of CO_2 and NH_3 formed with Pt/Al_2O_3. Fast hydrolysis of an intermediary cyanate on Al_2O_3 was already suspected by Voorhoeve et al. [35].

If this explanation is correct then differences in product distribution between Pt and Rh would result from the different amounts of NO and CO present on their surfaces. It is known that adsorbed CO is favoured on Pt [19,22–24] and adsorbed NO, or both species, is present on Rh [23,25,26]. Thus one would expect more N_2O to be formed (via reaction (19)) with Rh and more ammonia and CO_2 (via reactions (15), (16) and (17)) with Pt, as observed,

$$^*N + {}^*NO \rightarrow N_2O + 2* . \tag{19}$$

So far only the existence of the net reaction (7) has been proven. The proposed

Table 2
Turnover frequencies (TOF) of NO reduction on platinum

Catalyst	Conc. of CO, NO, H_2 (%)	TOF (s^{-1})
unsupported Pt–10%Rh [a]	5.0, 0.3, 0.5	31×10^{-3}
Pt/Al_2O_3 [b]	0.2, 0.2, 0.09	42×10^{-3}
Rh/Al_2O_3 [c]	0.2, 0.2, 0.24	96×10^{-3}

[a] Ref. [37]: 230°C, 70% conversion, total flow per metal surface area 2×10^4 ml h^{-1} m^{-2}.
[b] Present work: 210°C, 70% conversion, 64% dispersion.
[c] Present work: 210°C, 70% conversion, 28% dispersion.

Table 3
Product distribution with Pt/Al_2O_3 and Pt/SiO_2 using 2000 ppm NO and CO each and 890 ppm H_2 [a]. Catalyst weight (75 mg) and total flow rate (100 ml/min) were similar for both catalysts

Catalyst	Temp. (°C)	Conversion of NO (%)	Formation of NH_3 (ppm)	Formation of CO_2 (ppm)
Pt/Al_2O_3	210	42	520	550
Pt/SiO_2	210	28	100	200
Pt/SiO_2	230	45	220	300

[a] Data for Pt/SiO_2 were obtained by isothermal experiments with results being similar to temperature programmed reaction as given in figs. 1 and 2.

mechanism via isocyanic acid is based mainly on the conclusions drawn from the literature for the reaction of CO, NO and H_2 over unsupported noble metals. Convincing proof requires a demonstration that HNCO is a significant gas phase intermediate with supported catalysts of the type used here. If the acid exists, as subsequent work has indicated [39], then processes such as reaction (17) could be a valid explanation for the observed results under conditions involving CO, NO and hydrogen.

5. Conclusions

The addition of H_2 to mixtures of NO and CO causes large increases in the conversion of both NO and CO over Pt and Rh catalysts. A process which is described by the stoichiometric reaction $CO + NO + \frac{3}{2}H_2 \rightarrow CO_2 + NH_3$ comprises 50–100% of the additional reaction with Pt/Al_2O_3 and 20–50% with Rh/Al_2O_3. This process is believed to arise through formation of isocyanic acid on the metal followed by hydrolysis to CO_2 and NH_3 on the support.

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