# Hydrogen cyanide synthesis on polycrystalline platinum and 90:10 platinum-rhodium surfaces

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The synthesis of HCN from methane-based feedstocks has been studied at relatively low temperatures (up to 780 °C) and pressures (0.02–0.15 Torr) over both pure Pt and Pt–10%Rh alloy model catalysts. Steady-state synthesis of HCN is observed over Pt from  $CH_4-NH_3-O_2$  feed mixtures with a maximum in activity observed using a 1:1:0.5 mixing ratio. The activity of the Pt–10%Rh alloy under comparable conditions is significantly lower, indicating that Rh has an inhibiting effect on the synthesis reaction at these temperatures and pressures. Comparable steady-state levels of activity were not observed over Pt for pure  $CH_4-NH_3$ ,  $CH_4-NH_3-CO_2$  or  $CH_4-NO$  feed mixtures; in particular, for  $CH_4-NH_3$  feeds in the absence of oxygen a high initial activity was seen to decay rapidly over time. The effects of various surface pretreatments of the Pt were found to be transitory, with a gradual return of the HCN activity to its normal level in  $CH_4-NH_3-O_2$  (1:1:0.5) mixtures in all cases, and the most beneficial pretreatment effect was observed for a simple physical surface roughening induced by mild ion bombardment. By contrast, pre-exposure of the catalyst surface to ethylene or ammonia at elevated temperatures led to an initial inhibition or decrease in the synthesis activity.

# Introduction

The Andrussow process<sup>1</sup> is a long-established catalytic process for the industrial production of hydrogen cyanide, which involves the formation of HCN from a near equimolar mixture of CH<sub>4</sub>, NH<sub>3</sub> and O<sub>2</sub> at 1–2 atm over a 90:10 Pt : Rh (Pt–10%Rh) gauze catalyst under adiabatic conditions at *ca*. 1400 K and with very short contact times. The alternative Degussa process also employs a Pt-based catalyst but, in this case, the process is operated in the absence of oxygen using a CH<sub>4</sub>–NH<sub>3</sub> feed at yet higher temperatures and external heating provided by methane combustion.

Previous studies of these reactions have included pilot plant and laboratory scale reactor studies, detailed analyses of discharged catalyst gauzes and more fundamental surface science studies of the interaction of reactants, products and potential intermediates with platinum surfaces.<sup>2–7</sup> The detailed kinetics of HCN synthesis over Pt and Rh foils have also been studied at reduced pressures and the commercial process modelled by the group of Schmidt in Minnesota.<sup>8–11</sup> Despite this earlier work, however, there is still considerable uncertainty over the detailed role of Rh, the main synthesis pathways, the nature of the active catalyst surface and the identity of key surface intermediates.

In the approach adopted for the experiments described below, we have examined the synthesis reaction on model catalyst samples (flat polycrystalline foils) of pure Pt and a Pt-10%Rh alloy at relatively low pressure in a reaction cell attached to a surface analysis system. The advantages of this approach are that it permits the catalyst's surface temperature to be varied independently of the feed gas composition and flow rate, and for the reaction to be studied under conditions where the contribution of any homogenous processes and mass transport limitations are minimized. The state of the catalyst may also be accurately assessed, both prior to and after reaction, by the application of surface analytical techniques, and the catalyst may also be manipulated by the direct additions of controlled levels of poisons and promoters.

## Experimental

The apparatus used in these studies consisted of an ultra-high vacuum (UHV) surface analysis system equipped with a highpressure catalytic reaction cell. The analytical chamber itself was equipped for X-ray photoelectron spectroscopy (XPS), low-energy electron diffraction (LEED), Auger electron spectroscopy (AES) and temperature-programmed desorption (TPD): the XPS data reported below were obtained using Mg-K $\alpha$  radiation from a standard, non-monochromated X-ray source and a VG-CLAM2 100 mm hemispherical analyser which was operated in a fixed pass-energy mode for a given spectral region (50 eV for C 1s, O 1s and N 1s; 20 eV for Pt 4f and Rh 3d). The spectrometer was calibrated using a Cu–Au reference sample and spectra were acquired at normal emission angles; quoted binding energies are taken directly from the intensity maxima of the raw data.

Samples could be transferred directly from the main UHV system into the high-pressure reaction cell using a magnetically coupled translator. This reaction cell could be isolated from the main chamber by a gate valve and separately pumped by a liquid-nitrogen trapped diffusion pump; in normal operation pumping was via a high-conductance valve but for reaction studies pumping was normally limited to a low conductance bypass with in-line regulating valve. The reactor gas feed was pre-mixed in a special high vacuum chamber connected to the main gas-handling line. The inlet bleed valve from this chamber to the reaction cell and the aforementioned pump regulation valve together provided control over both the gas pressure and gas residence time in the reactor. At the pressures employed in this study (typically 0.02-0.15 Torr) the reactor is best regarded as having characteristics approaching those of a continuously stirred tank reactor and the gas residence time has been estimated from the half-life of reaction products in the cell when the reaction is quenched by rapid cooling of the sample. The cell was also connected through a finer flow control valve to a differentially pumped quadrupole mass spectrometer and heating was applied to maintain the whole of this gas inlet system at ca. 50 °C to prevent product condensation. Mass spectrometric

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data were recorded in a multiple-ion monitoring mode in which the sample temperature and the intensities of up to 15 mass fragments were monitored quasi-simultaneously. The products that were routinely monitored in addition to HCN were  $H_2$ ,  $H_2O$ ,  $CO-N_2$ , NO and  $CO_2$ ; no partial oxidation products of any further reactions of HCN (such as urea or formamide) were detected.

The model catalysts employed for this work consisted of strips of platinum foil (Advent Research Materials: 0.015 mm thick, >99.95%) and platinum-rhodium foil (Johnson Matthey: 90%Pt-10%Rh, 0.0125 mm thick, >99.9%) cut to a size of ca.  $1 \times 2$  cm<sup>2</sup> and supported between Ta mounts on gold-coated stainless-steel holders. The sample was heated resistively by an ac supply and the temperature governed using a Newtronic Micro 96 programmable controller. The temperature was measured using a chromel-alumel thermocouple, spot-welded directly onto the back of the sample. Care was taken to ensure that the resistive heating did not influence the thermocouple reading and the stability of the thermocouple reading over time was also verified by using a large-area photovoltaic detector mounted externally on a borosilicate window to measure the intensity of the black-body radiation emitted at set temperatures. This showed a drift of the sample temperature measurement of no more than 5 °C over the six months of operation.

The samples were initially cleaned by cycles of 500 eV argon-ion bombardment (*ca.* 5  $\mu$ A, 20 min) and vacuum annealing at 700 °C, until only low levels of carbon and oxygen impurities were apparent. The samples were finally cleaned by high-temperature oxygen treatment and, indeed, this was routinely used as the final treatment prior to a catalytic run. The exact procedure for cleaning in oxygen varied according to the sample: platinum was heated in a dynamic flow of oxygen (>10<sup>-7</sup> Torr) at 700 °C for 10 min, cooled to below 100 °C under oxygen and then reheated to 750 °C for 2 min in UHV to desorb any adsorbed oxygen. For the platinum–rhodium alloy, oxidation of the rhodium by oxygen at moderate temperatures was a concern, so the catalyst was heated in oxygen (>10<sup>-7</sup> Torr) to 700 °C for 5 min and then held at this temperature whilst the oxygen was evacuated for a further 5 min in UHV.

The standard conditions employed for a reactor experiment, to be assumed unless stated otherwise, were a total gas pressure of 0.10 Torr, a gas residence time of 5.7 s and a catalyst surface temperature of 600 °C. The standard reaction feed was a mixture of CH<sub>4</sub>-NH<sub>3</sub>-O<sub>2</sub> in a 1:1:0.5 mole ratio. The heating was adjusted such that the sample would be brought from room temperature to within 5 °C of the desired reaction temperature in less than 25 s, with minimal overshoot. Cooling of the sample to below 300 °C (where reaction had ceased) occurred in a matter of seconds; the stabilisation of the mass spectrometer readings was then dependent on the gas residence time. In the absence of oxygen, steady-state synthesis activity was not observed under the normal conditions of temperature and pressure employed in this work; instead an initial surge of products was followed by a gradual reduction with time.

Mass spectrometer signals were shown to be linear with reactor partial pressure over the experimental range using a calibrated mixture of  $5.03 \pm 0.05\%$  CO<sub>2</sub> in nitrogen (Air Products plc). The sensitivity of the detection system to CO<sub>2</sub>, HCN and CH<sub>4</sub> (all relative to N<sub>2</sub>) was determined using the aforementioned CO<sub>2</sub> mixture, a calibrated mixture of  $0.98 \pm 0.03\%$  HCN in nitrogen (MG Gas Products Ltd.) and a 50 : 50 mixture of CH<sub>4</sub> in N<sub>2</sub> (prepared *in situ*). These data were then used to determine the relative sensitivities of the product gases HCN and CO<sub>2</sub> relative to CH<sub>4</sub> and the yields quoted in this work are derived from comparison of the product signal with the CH<sub>4</sub> signal immediately prior to initiation of the reaction; the quoted yields are thus based on carbon (CH<sub>4</sub>) conversion to the specified product and the internal calibration negates the effects of any experimental drift in absolute intensities over time. The main drawback of the use of mass spectrometric analysis is the inability to discriminate between CO and  $N_2$  (given that the characteristic 12, 14 and 16 fragment ion signals also overlap with those from other species) and for this reason we do not report any direct data on these particular products.

# Results

#### **Polycrystalline Pt samples**

The sample surface was routinely examined by XPS to check its cleanliness before reaction and examined after reaction at both room temperature and 250 °C. Post-reaction analysis commonly showed very little surface nitrogen (a very weak peak at ca.  $399.5 \pm 0.5$  eV; removed by heating to 250 °C), oxygen, almost exclusively as CO, (giving an O 1s peak at ca. 532.6 eV; heating to 250 °C removed this peak and gave a 28 u desorption signal) and carbon as both CO (at 285.3 eV) and an apparently elemental, less volatile form giving rise to a C 1s peak at ca. 284.3 eV. Re-exposure of the surface to CO at low pressures after it had been heated to 250 °C did not, however, generate the same levels of surface carbon and oxygen seen after the sample was first removed from the reactor; this suggests that the treatment at 250 °C itself induces changes in the nature of the Pt surface and that perhaps the reactive surface is unstable in the absence of stabilising adsorbates.

In general, there was no obvious correlation between the reaction conditions employed and the amount of elemental carbon detected in the subsequent post-reaction analysis of the surface, which would correspond to a near-monolayer coverage on the freshly cleaned and annealed Pt surface. It should be noted, however, that all samples were cooled from the reaction temperature under the reactant gas mixture and the surface being examined in the post-reaction analysis cannot therefore be considered to be truly representative of that existing under steady-state synthesis conditions.

**Transient behaviour during reaction initiation.** Fig. 1 shows a typical set of raw data illustrating the initial stages of a reaction run. The stabilisation of the mass readings is principally dependent on stabilisation of the sample temperature. The main exception to this is the 18 u peak, which takes slightly longer to stabilise, indicating some degree of water retention in the gas inlet system despite the applied heating; however, the signals of all species had reliably stabilised well within the standard run time of 5 min.

There is transient production of both NO and  $CO_2$  during the initiation stages at levels which, although small, are still noticeably higher than those observed at steady state. The signals of a number of masses, but most noticeably hydrogen, exhibit initial oscillations, but these are merely a direct reflection of similar oscillations in the sample temperature as it approaches its set-point value.

Effect of gas residence time  $(1:1:0.5 \text{ CH}_4-\text{NH}_3-\text{O}_2)$ . The variation of HCN yield with gas residence time over platinum at 600 °C is shown in Fig. 2; an initial near-linear rise in yield with residence time begins to level off after *ca*. 10 s. Prior to this point, the extent of the synthesis reaction is clearly controlled by the gas residence time and the measured steady-state yield of HCN is principally determined by the kinetics of the initial synthesis reactions, whereas at longer residence times the HCN yield is beginning to be affected by either thermodynamic equilibrium limitations or by the onset of serial reactions, such as hydrolysis, in which HCN is consumed. A change in either the total pressure (a reduction to 0.02 Torr) or in the temperature (to 700 °C) leads to a change in the per-



**Fig. 1** Initial stages of reaction; raw mass spectral data for a standard run over Pt with a  $1:1:0.5 \text{ CH}_4\text{-}\text{NH}_3\text{-}\text{O}_2$  feed at 0.10 Torr total pressure (the sample heating to 600 °C is initiated at t = 60 s)

centage yield, but not in the basic form of the graph, nor to a significant change in the residence time at which the HCN yield begins to plateau. In view of these results, all further studies of the synthesis kinetics used a constant (standard) residence time of 5.7 s.

Effect of catalyst temperature  $(1:1:0.5 \text{ CH}_4-\text{NH}_3-\text{O}_2)$ . A change in the sample surface temperature has a significant



Fig. 2 Variation of the HCN yield with gas residence time over the Pt sample  $(1:1:0.5 \text{ CH}_4\text{--}\text{NH}_3\text{--}\text{O}_2, 600 \,^\circ\text{C}, 0.10 \text{ Torr})$ 

effect on the HCN yield, as would be expected for any heterogeneously catalysed process; we would note at this point that the incident gas temperature will be substantially lower than the surface temperature under all our operating conditions. The variation of HCN yield with catalyst temperature for platinum at 0.10 and 0.02 Torr is shown in Fig. 3 (together with similar data for the platinum-rhodium alloy at 0.10 Torr, which is discussed below). There is no catalytic production of HCN at 300 °C or below, but the yield then shows a steady increase from 400 to 700 °C. The percentage HCN yield from platinum is similar at the two pressures, indicating that HCN formation is approximately first order with respect to total pressure for a 1:1:0.5 mix of NH<sub>3</sub>-CH<sub>4</sub>-O<sub>2</sub> under our conditions. At the highest temperatures the activity apparently starts to decrease at the higher pressure, but this is likely to be due to the onset of further reactions in which HCN is consumed. We would further note that, of the various other products, hydrogen shows a particularly strong dependence of yield on substrate temperature.

Variation of the CH<sub>4</sub>-NH<sub>3</sub>-O<sub>2</sub> feed ratios. In the industrial process, a key role of oxygen is to provide, through combustion, sufficient heat to maintain the otherwise endothermic conversion of CH<sub>4</sub> and NH<sub>3</sub> into HCN and H<sub>2</sub>. In the Andrussow process, oxygen is mixed directly with these gases, in the Degussa process the reaction gases are heated externally by the combustion of methane. In the experimental conditions used in this study the catalyst was heated electrically so, as mentioned previously, the oxygen concentration could be varied without affecting the catalyst temperature. The partial pressures of NH<sub>3</sub> and CH<sub>4</sub> were, however, kept equal to each other, and the overall reaction pressure was maintained constant at 0.10 Torr. The yields of HCN and CO<sub>2</sub> (expressed as % conversion of methane), and the total % conversion of methane are listed in Tables 1–3.

Increasing the relative concentration of oxygen by changing the feed composition from the standard 1:1:0.5 mixture to 1:1:1 (CH<sub>4</sub>-NH<sub>3</sub>-O<sub>2</sub>), whilst maintaining the same total



**Fig. 3** Variation in the HCN yield from a 1:1:0.5 CH<sub>4</sub>-NH<sub>3</sub>-O<sub>2</sub> feed mixture with the catalyst temperature: (a) Pt sample (1:1:0.5 CH<sub>4</sub>-NH<sub>3</sub>-O<sub>2</sub>, 0.02 Torr); (b) Pt sample (1:1:0.5 CH<sub>4</sub>-NH<sub>3</sub>-O<sub>2</sub>, 0.10 Torr); (c) Pt-10%Rh sample (1:1:0.5 CH<sub>4</sub>-NH<sub>3</sub>-O<sub>2</sub>, 0.10 Torr); (d) Pt-10%Rh sample (1:1:0.5 CH<sub>4</sub>-NH<sub>3</sub>-O<sub>2</sub>, 0.10 Torr)

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 Table 1
 Steady-state yield (%) of HCN over platinum at different temperatures and gas compositions

	gas feed (CH <sub>4</sub> -NH <sub>3</sub> -O <sub>2</sub> )			
temperature/°C	1:1:0	1:1:0.1	1:1:0.5	1:1:1
600 700	Ļ	↓ 7.2(65)	10.2(44) 10.5(33)	0.0(0) 4.0(18)
750	Ì	8.2(37)	9.1(26)	7.2(22)

All at a total pressure of 0.10 Torr. HCN selectivity, given in brackets, is based upon methane consumption.  $\downarrow$ : Decays with time.

pressure of 0.10 Torr, reduces the HCN yield and selectivity, whilst increasing the production of  $CO_2$ ,  $H_2O$  and, by implication, CO. The reduced HCN production is most marked at the lowest temperature studied, 600 °C, where no HCN yield is detected using the 1:1:1 feed. At higher temperatures the production of HCN recovers, reaching almost 80% of the amount produced by the standard mixture at 750 °C. CO<sub>2</sub> production at 600 °C is about eight times higher using the more oxygen-rich mixture. This increase in the oxidation products of CH<sub>4</sub> as the oxidant concentration increases is unsurprising, but both mixtures also show a reduction in CO<sub>2</sub> with increasing temperature. This decrease in CO<sub>2</sub> yield is likely to reflect increasing selectivity to CO (in part, at least, since the thermodynamics increasingly favour CO at these higher temperatures) but we are unable to confirm this directly owing to the aforementioned signal overlap in the mass spectra. The trends observed in switching from the standard mixture to the 1:1:1 mixture were further enhanced when 1:1:1.5 mixtures were employed.

The link between oxygen concentration and production of  $CO_2$  also persists when the oxygen concentration is reduced, in that a 1:1:0.1 ratio  $CH_4$ - $NH_3$ - $O_2$  mixture produces no discernible  $CO_2$ . Relative to the standard 1:1:0.5 feed mixture, the HCN yield from the 1:1:0.1 mixture is slightly lower at high temperatures, although the selectivity to HCN is noticeably higher. However, at 600 °C the HCN yield from this more oxygen-lean mixture does not remain constant, but shows a gradual decline after the first minute. This latter result implies that the catalyst surface at 600 °C is either being poisoned by a build-up of reaction by-products, which are not now being removed sufficiently rapidly by oxidation, or that a surface restructuring is occurring in the more reducing atmosphere to give a non-catalytic surface. Thus the chemical potential of oxygen must be insufficient either to oxidise the

Table 2 Steady-state yield (%) of  $\text{CO}_2$  over platinum at different temperatures and gas compositions

	gas feed (CH <sub>4</sub> -NH <sub>3</sub> -O <sub>2</sub> )			
temperature/°C	1:1:0	1:1:0.1	1:1:0.5	1:1:1
600	0.0	0.0	0.5	4.1
700 750	0.0 0.0	0.0 0.0	0.5 0.2	1.3 0.9

All at a total pressure of 0.10 Torr.

 Table 3
 Methane conversion (%) over platinum at different temperatures and gas compositions

temperature/°C	gas feed (CH <sub>4</sub> -NH <sub>3</sub> -O <sub>2</sub> )			
	1:1:0	1:1:0.1	1:1:0.5	1:1:1
600 700 750	$\downarrow \\ \downarrow$	↓ 11.1 22.2	23.2 32.0 34.7	11.1 22.2 33.3

All at a pressure of 0.10 Torr.  $\downarrow$ : Decays with time.

impurities or to stabilise the catalytic surfaces at this lower temperature and partial pressure.

In the complete absence of oxygen (anoxic conditions), a 1:1 ratio of CH<sub>4</sub> and NH<sub>3</sub> does not produce a significant steady-state yield of HCN under our conditions at any temperature up to 750 °C. Instead, there is an initial transient production of HCN but the synthesis rate then gradually decays to a near-zero value. The main products of this reaction (albeit again only transiently) are H<sub>2</sub> and N<sub>2</sub> which are initially produced in very high yield, a feature which is reflected in the NH<sub>3</sub> consumption which temporarily approaches 50% at 750 °C. In general, the decay in HCN yield is more pronounced at higher temperatures and this is illustrated in the typical profiles of the HCN yield against time shown in Fig. 4. However, it is important to note that the exact form of the profile must be treated with caution because, at a set temperature, it is dependent to some extent on the rate of heating to that temperature: the faster the heating, the more rapid the initial decay in yield. Nevertheless, it appears that the rate of decay of HCN production is in general rather faster than that of H<sub>2</sub> and N<sub>2</sub>. No transient production of HCN, H<sub>2</sub> or N<sub>2</sub> was evident when the same samples were re-tested without cleaning, indicating that the decay in synthesis activity seen in the first run cannot be simply reversed by an evacuation treatment or by cooling and re-heating to reaction temperature.

Increasing the CH<sub>4</sub> to NH<sub>3</sub> ratio from 1:1 to 2:1 simply exacerbated the effects reported above; a slightly smaller transient yield of HCN was again followed by a rapid decay in activity to a near-zero limiting value. By contrast, increasing the NH<sub>3</sub> concentration by changing the CH<sub>4</sub> to NH<sub>3</sub> ratio from 1:1 to 1:2 did not substantially affect the behaviour, with the exception that an anomalously high 29 u signal was evident in some experiments. In the experiments of concern, the analysis system was modified so that the mass spectrometer could sample gas from the reactor more directly. Comparison of the 29/28 u signal intensity ratio across a range of such experiments indicates a definite trend with the value increasing from 2-5% in standard  $CH_4$ -NH<sub>3</sub>-O<sub>2</sub> (1:1:0.5) runs, to around 10% in some 1 :1 CH<sub>4</sub>-NH<sub>3</sub> runs and as high as 24% during the high transient activity initially observed in 1:2 CH<sub>4</sub>-NH<sub>3</sub> runs. Analysis of the complete fragmentation pattern suggests that the species responsible for this 29 u



**Fig. 4** Transient HCN production from a  $1:1 \text{ CH}_4\text{-NH}_3$  feed mixture over platinum at 0.10 Torr. (----) 750, (-----) 700 and (.....) 600 °C.

signal might be  $H_2C=NH$ , but further work is required to confirm that it is indeed this species which is responsible and that it is a real product of the catalytic reaction over Pt rather than an artifact of the modified analysis system.

Use of alternative oxidants and CH<sub>4</sub>-NO feed mixtures. From the preceding section, it is clear that an oxidant of some form is required to maintain HCN synthesis activity under our accessible operating conditions of temperature and pressure; in this section we therefore report briefly on the use of the alternative reactant mixtures; (i)  $CH_4$ -NH<sub>3</sub>-CO<sub>2</sub>, and (ii)  $CH_4$ -NO.

At high temperatures we would anticipate  $CO_2$  could act as a mild oxidant and could thus be capable of removing surface carbon by means of the reverse Boudouard reaction.

$$C + CO_2 \rightarrow 2CO$$

It is also possible that the direct addition of  $CO_2$  (and through its action as an oxidising agent, also CO) might positively enhance the equilibrium HCN yield by its influence on the equilibrium positions of the various reactions in which  $CO_x$  are produced (including the direct partial oxidation of methane and HCN hydrolysis); indeed, it has been previously claimed that the yield of HCN may be increased by addition of  $CO_2$  to the standard reaction mixture.<sup>12</sup>

Our results, obtained using a 1:1:1 mixture of CH<sub>4</sub>, NH<sub>3</sub> and  $CO_2$ , are shown in Fig. 5 for a total pressure of 0.15 Torr; the partial pressures of NH<sub>3</sub> and CH<sub>4</sub> are thus the same as for the measurements shown in Fig. 4. It is immediately clear that this addition of carbon dioxide does not permit steady state synthesis to be maintained, even at  $750 \,^{\circ}\text{C}$  (*i.e.* at conditions under which a high HCN yield is obtained with a 5% oxygen component in the feed mixture); there is, however, a slight improvement relative to a 1:1 CH<sub>4</sub>-NH<sub>3</sub> feed, in that the rate of activity loss is noticeably reduced. Rather surprisingly, the trend in behaviour with temperature is also different from that initially anticipated in that the addition of  $CO_2$  to the 1:1  $CH_4$ -NH<sub>3</sub> mixture has only a very small apparent effect at 750 °C, but does result in a much more pronounced reduction in the rate of decay of synthesis activity at lower temperatures. The mass spectra show that small amounts of carbon dioxide (initially ca. 6-8%, but reducing

with time) are consumed at each reaction temperature. There is no detectable water production (18 u) and whilst there is a substantial 28 u signal, this can largely be attributed to nitrogen produced by  $NH_3$  decomposition rather than CO, and there is a concomitant increase in the  $H_2$  signal.

The synthesis of HCN from CH<sub>4</sub>–NO feeds (1 :1 and 1 : 2) was also briefly studied. At temperatures of 600–650 °C an initial transient production of a low level of HCN was followed by a slow decay to a very low level of activity. At higher temperatures (700–750 °C) steady-state HCN production was observed but the activity was typically a factor of 5–10 lower than that seen from CH<sub>4</sub>–NH<sub>3</sub>–O<sub>2</sub> (1 :1 : 0.5) mixtures under comparable conditions. In all cases the main products of the reaction were CO–N<sub>2</sub> and H<sub>2</sub>O with only a very low production of H<sub>2</sub> evident. The reactions of CH<sub>4</sub>–NO feed mixtures were also characterised by a particularly high transient production of CO<sub>2</sub> during the first 10–20 s of the reaction and a significant steady-state yield of CO<sub>2</sub> throughout the remaining course of reaction.

Effect of surface pretreatments  $(1:1:0.5 \text{ CH}_4-\text{NH}_3-\text{O}_2)$ . The effect of the pre-existing surface condition of the sample on the initial activity and subsequent evolution of the catalytic behaviour was investigated in a series of experiments in which the sample was first cleaned in the standard fashion and then subjected to one of various pretreatments prior to exposure to reaction conditions. The main pretreatments employed were: (i) a brief argon-ion bombardment of 5 min (500 eV, 5  $\mu$ A); (ii) an extended argon-ion bombardment of 20 min, followed by a 250 °C anneal; (iii) exposure to two aliquots of 201 of ethylene with the sample held at 600  $^{\circ}$ C; (iv) exposure to 60 l of oxygen at 323 °C; (v) an ammonia pretreatment in the reaction chamber which involved heating the catalyst to 700 °C for 5 min in pure ammonia (0.05 Torr). The subsequent reactivity tests all used the standard gas mixture (1:1:0.5  $CH_4-NH_3-O_2$ ) at the standard temperature (600 °C) and pressure (0.10 Torr).

The effects of the five different pretreatments on the catalytic behaviour are compared directly with the results of a standard run in Fig. 6. It is immediately apparent from this figure that, whilst the pretreatments did have an influence on

18



16 14 12 HCN yield (%) 10 8 6 4 2 0 0 200 400 600 800 time / s

**Fig. 5** Transient HCN production from a  $1:1:1 \text{ CH}_4\text{-NH}_3\text{-CO}_2$  feed mixture over platinum at 0.15 Torr. (----) 600, (....) 700 and (\_\_\_\_) 750 °C.

**Fig. 6** Activity of a Pt foil (standard conditions; 1:1:0.5 CH<sub>4</sub>–NH<sub>3</sub>–O<sub>2</sub>, 600 °C, 0.10 Torr) subjected to the following pretreatments: (a) brief ion bombardment, (b) extended ion bombardment and 250 °C vacuum anneal, (c) ammonia, (d) oxygen, (e) standard, (f) ethylene (see text for further details)

The initial HCN yield was accentuated after both argon ion bombardment routines, albeit to different extents, suggesting that the surface roughening which this treatment will have caused had a significant effect on the catalytic performance. The highest HCN yield was produced after a brief (5 min) bombardment period; the long (20 min) bombardment was followed by heating to 250 °C for 5 min, and this vacuum annealing apparently reduced the roughening effect by more than was gained by prolonging the bombardment. The increase in HCN yield in these experiments is not, however, a result of substantially enhanced CH<sub>4</sub> conversion but reflects a significant increase in selectivity to HCN. Both the HCN yield and selectivity from the pretreated surfaces decreased over time and tended towards that from the standard run, a behaviour which is entirely consistent with a gradual loss of surface roughness.

Previous results from the anoxic runs (see above) have suggested that carbon accumulation was responsible for loss of catalytic activity. Pretreatment of the sample by twice exposing the hot (600 °C) surface to 20 1 of ethylene gave a heavy carbon deposit characterised by an intense XPS C 1s peak at 284.5 eV; the XPS results therefore suggest a carbon deposit similar in nature to those of post-reaction analyses, but the peak is over five times more intense. Despite all this initial surface carbon, the effect on the HCN yield from the oxygencontaining feed mixture was relatively mild. There was a slight retardation of the onset of HCN synthesis but the yield nevertheless rapidly attained a value only slightly (ca. 20%) lower than that seen in the standard run, and this difference then lessened with time. Correspondingly, there was a very small rise in the yield of CO<sub>2</sub> compared to the standard run (in absolute terms, up 0.05%) but despite this the HCN selectivity was very similar to that in the standard run, which indicates CO production is also reduced. Overall, therefore, ethylene pretreatment slightly inhibits both HCN synthesis and methane oxidation. Post-reaction XPS analysis revealed that over 80% of the initially deposited carbon had been burnt off during the single 5 min run and the final level of surface carbon was comparable to that seen after any run employing these reaction conditions.

As might be expected on the basis of the above results, preexposure of the Pt surface to ethylene under milder conditions, designed to give a near-saturation overlayer of surface ethylidyne, had very little effect on the HCN activity, with the exception that a slight retardation of the onset of HCN synthesis was again evident.

The platinum was pretreated with ammonia under conditions (0.5 Torr,  $700^{\circ}$ C) where the platinum can effectively catalyse the decomposition reaction. However, during this treatment the catalytic activity towards NH<sub>3</sub> decomposition dropped by ca. 80%, suggesting either that surface rearrangement or site blocking was occurring (this reaction is known to be very structure sensitive on Pt<sup>13</sup>). Subsequent XPS analysis revealed at best only a slight accumulation of nitrogen on the surface, with a very weak peak at ca. 400 eV, which would apparently rule out stabilisation of a catalytically inactive surface state by adsorbed nitrogen species, although the possibility that the same effect might be induced by adsorbed hydrogen cannot be excluded. Some adventitious CO adsorption was evident and it is possible that the CO masked other, less abundant surface carbon species. The effect of this pretreatment was to give an initial period of inhibition of HCN production but an increase in initial CO<sub>2</sub> and NO formation, followed by a rapid rise in HCN yield and a drop in the oxidation products to the levels found in the standard run. The mild oxidation pretreatment employed (exposure to

 $10^{-7}$  Torr O<sub>2</sub> for 10 min at 323 °C) was less severe than that

normally employed for cleaning the platinum catalyst, but whereas the standard oxygen cleaning treatment is followed by heating *in vacuo* to remove adsorbed oxygen, this procedure was a way of restoring the adsorbed oxygen and gave an O 1s XPS peak at 529.8 eV. Perhaps unsurprisingly, this pretreatment gave results showing no difference within experimental error from those of a standard run.

## Polycrystalline Pt-10% Rh samples

The composition of the freshly bombarded platinum-rhodium alloy surface was investigated by XPS using two methods: the first was a comparison of the absolute platinum  $4f_{7/2}$  peak intensity from the alloy with that from the pure metal whilst the second involved a comparison of the platinum  $4f_{7/2}$  and rhodium 3d<sub>5/2</sub> peaks, solely from alloy spectra. The first method did not give particularly good reproducibility and was susceptible to even slight amounts of surface contamination and slight variation in the detector sensitivity over time, but after correction for these factors this method gave results indicating a platinum concentration in the alloy to be 91% or more of that in pure platinum. The second method, involving a direct comparison of two different signals from the same alloy, is not affected by such factors, but does require information concerning the relative sensitivities of the two signals. Published empirical sensitivity factors would suggest an absolute concentration of 86% or less platinum.<sup>14</sup> In view of the errors inherent in both methods, it seems reasonable to accept that the surface composition of the alloy is indeed close to the bulk composition of 90.0% platinum-10.0% rhodium certified by the manufacturer.

Irrespective of the absolute surface stoichiometry, we would stress that the platinum to rhodium signal ratio observed for the alloy immediately after ion bombardment was found to be unchanged following annealing (to  $750 \,^{\circ}$ C) or cleaning in oxygen ( $10^{-7}$  Torr,  $700 \,^{\circ}$ C). The only occasions when this internal signal ratio varied was under reducing conditions, and this effect could be reversed by reoxidation (this feature is more fully discussed below). To quantify these changes in surface stoichiometry under reaction conditions, the concentration of each metal was determined from the integrated peak areas of the fitted XPS data after subtraction of a Shirley background.

The catalytic activity of the Pt–10%Rh alloy towards HCN and CO<sub>2</sub> production, and methane conversion is detailed in Tables 4–6, whilst the variation of activity with temperature under standard conditions is compared directly with that for pure platinum in Fig. 3. We would wish to emphasize, however, that the activity of the Pt–10%Rh surface (unlike the pure Pt) is very susceptible to variations in the sample history, *i.e.* the sample exhibits a relatively long-lasting memory effect which can influence the catalytic activity observed in any given experimental run and can lead, for example, to hysteresis type effects in sequential measurements. The 1:1:0.5data of Tables 4–6 and curve (c) of Fig. 3 were, for example, recorded sequentially, in strict order of decreasing temperature and the activities thus recorded at temperatures of 700 °C and below are significantly higher than would have

**Table 4**Steady-state yield (%) of HCN over a 90% platinum-10%rhodium alloy at different temperatures and gas compositions

	gas feed (CH <sub>4</sub> -NH <sub>3</sub> -O <sub>2</sub> )			
temperature/°C	1:1:0	1:1:0.25	1:1:0.5	1:1:1
600 700 750	$\downarrow \downarrow \downarrow$	2.6(31) 4.2(31) 4.8(36)	1.3(11) 3.2(26) 3.9(21)	0.0(0)

All at a total pressure of 0.10 Torr. HCN selectivity, given in brackets, is based upon methane consumption.  $\downarrow$ : Decays with time.

**Table 5**Steady-state yield (%) of  $CO_2$  over a 90% platinum 10 %rhodium alloy at different temperatures and gas compositions

		gas feed (CH <sub>4</sub> -NH <sub>3</sub> -O <sub>2</sub> )			
temperature/°C	1:1:0	1:1:0.25	1:1:0.5	1:1:1	
600 700	0.0	0.6	2.2	21	
750	0.0	0.2	0.5	21	

All at a total pressure of 0.10 Torr.

been recorded in runs in which the reaction had previously been operated at lower temperatures; this characteristic of the reaction on Pt–10%Rh is the origin of the apparently anomalous 600 °C data point in curve (d) where the data were recorded after operation at a lower temperature. In summary, we would note that treatment of the Pt–10%Rh sample in the reaction mixture at a high temperature enhances the activity of the sample in subsequent measurements at lower temperatures and that this effect can be quite long-lasting and lead to some apparent irreproducibility in the activity measurements.

Nevertheless, under all the conditions where a direct comparison has been made, the Pt-10%Rh alloy sample gave a significantly lower yield of HCN than did the pure platinum sample. The yield (and selectivity) of HCN was higher when a more oxygen lean mixture was employed, but still did not approach that obtained over pure Pt. Furthermore, under the more oxidising environment of a 1:1:1 CH<sub>4</sub>-NH<sub>3</sub>-O<sub>2</sub> feed at 700 °C the HCN production was below our detection levels, whilst oxidation products of NH<sub>3</sub> and CH<sub>4</sub> were in abundance, with large rises in the 44 (CO<sub>2</sub>), 30 (NO), 28 (CO) and 18 (H<sub>2</sub>O) u signals. Having shown that the introduction of rhodium promotes only oxidative catalysis under these more oxygen-rich conditions, no further experiments were conducted at a feed ratio of 1:1:1.

After reaction, the Pt-10%Rh surface exhibited a slightly higher surface concentration of N-containing species than was found to be the case with pure Pt, with weak peaks evident at 399.4 ( $\pm$ 0.2) and 397.3 ( $\pm$ 0.2) eV. TPD measurements on Pt-10%Rh samples freshly transferred from the reactor, clearly exhibited near-coincident HCN and H<sub>2</sub> desorption in addition to the major 28 u (CO) peak.

When the Pt–10%Rh sample is operated under anoxic conditions, with a 1:1 feed mixture of  $NH_3$  and  $CH_4$ , the catalyst loses activity in the same manner as is seen for pure platinum, but the very low ultimate yields of the two catalysts are comparable (in contrast to the reduced yield from the alloy in the presence of oxygen). Once again, the rate of loss of catalytic activity is greater at higher temperatures. In this case, however, another effect also manifests: the ratio of platinum to rhodium in the surface region decreases with time of operation of the catalyst in the anoxic environment. These changes have been followed by XPS, which enables the degree of change within the sampled surface region to be clearly established, although it does not permit determination of an absol-

**Table 6** Methane conversion (%) over a 90% platinum-10%rhodium alloy at different temperatures and gas compositions

	gas feed (CH <sub>4</sub> -NH <sub>3</sub> -O <sub>2</sub> )			
temperature/°C	1:1:0	1:1:0.25	1:1:0.5	1:1:1
600 700	Ļ	8.4 13.5	12.1 12.5	22.9
750	ţ	13.5	18.9	

All at a total pressure of 0.10 Torr.

ute change in concentration in the topmost surface layer. The manner in which the ratio of rhodium  $3d_{5/2}$  peak area to platinum  $4f_{7/2}$  peak area changes with reaction time at various reaction temperatures is shown in Fig. 7, which clearly shows how the surface composition tends to a new limiting value which is essentially independent of the reaction temperature.

The decay of catalytic activity with a 1:1 mixture, as measured by the decrease of product peaks in the mass spectra (both HCN at 27 and 26 u and N<sub>2</sub> and H<sub>2</sub>, from NH<sub>3</sub> decomposition, at 28 and 2 u), is virtually exponential over many minutes and, furthermore, the rate of this decay is apparently not dependent on the sample history. This indicates that the process causing the decay in activity is pseudo-first order in this region, and apparent rate constants for the decay in activity can therefore be derived without knowledge of the absolute concentrations. If the rate of rhodium enrichment in the surface region is also assumed to be first order then kinetic data can also be derived for this segregation process for comparative purposes. Thus the rates of change of surface composition at the various reaction temperatures can be determined and these values can be used to determine an activation energy for the surface enrichment. Arrhenius plots for the decay in the rates of HCN synthesis and ammonia decomposition, and for rhodium enrichment are shown in Fig. 8, from which the corresponding activation energies are 76(±15), 79(±17) and 123(±19) kJ mol<sup>-1</sup> respectively. The similarity in values for the two catalytic reactions suggests that the loss of catalytic activity is due to the same cause in both cases. This is to be expected for such similar reactions. The rhodium enrichment occurs with a completely different activation energy, showing that the loss of catalytic activity cannot simply be related to the change in surface composition of the catalyst.

The effect of surface pretreatments on HCN yield for the Pt-10%Rh alloy have been studied in a similar fashion as for pure Pt. Most notably, the argon-ion bombardment pretreatments have similar effects in platinum and the alloy, although for the Pt-10%Rh alloy the longer ion bombardment procedure (with subsequent 250 °C anneal) gave the highest initial activity. Our results for the chemical pretreatments are,



**Fig. 7** Change in the Rh  $3d_{5/2}/Pt 4f_{7/2}$  XPS signal ratio with time of exposure to a  $1:1 \text{ CH}_4$ -NH<sub>3</sub> feed mixture at 0.10 Torr. (----) 750, (...) 700, (...) 650 and (...) 600 °C.



Fig. 8 Arrhenius plots for the surface enrichment of rhodium and associated reactions on a Pt-10%Rh sample: (a) decay of HCN synthesis activity; (b) decay of ammonia decomposition activity; (c) surface enrichment of rhodium

however, complicated by the effects of sample history discussed above, and for this reason we will mention only the most pertinent observations.

Little difference was found between a standard run and one after ethylene pretreatment. The rate of recovery of catalytic activity thus appears to be better than for platinum, even though XPS reveals the initial level of surface carbon and the reduction to a residual carbon level during the reaction to be similar.

NH<sub>3</sub> pretreatment gave a change in the rhodium/platinum ratio at the alloy surface, as found for the anoxic CH<sub>4</sub>-NH<sub>3</sub> mixtures. After such pretreatment, the initial HCN production from the standard mixture is very low and only increases slowly towards that observed after the normal sample pretreatment. Although we have previously noted that there is not a simple correspondence between Rh surface segregation and activity decay, the slow increase in activity seen in this instance does seem to be related to the gradual increase in Pt: Rh ratio as it reverts back from that produced by the NH<sub>3</sub> pretreatment. However, the catalyst surface had still not completely restored its concentration to that before pretreatment, even after 10 min in the standard gas mixture at 600 °C. The initial production of NO (and to a lesser extent  $CO_2$ ) was again more pronounced than in a standard run, as it was for platinum after ammonia pretreatment. Pretreatment with a 1:1 mixture of  $NH_3$  and  $CH_4$ , which gave both surface carbon deposits and a change in Pt: Rh ratio, gives results superimposable with those of NH3 pretreatment, thus confirming restoration of the initial ratio and not removal of carbon deposits to be the significant factor in the improving catalytic activity.

Oxygen pretreatment of the alloy was carried out under various conditions, including treatment at  $327 \,^{\circ}$ C in  $10^{-7}$  Torr of oxygen (under which conditions sub-surface incorporation and/or surface oxides formation are known to occur on rhodium<sup>15,16</sup>) which gave a substantially more intense O 1s XPS peak at 529.8 eV on the alloy surface than was previously found for pure Pt. No surface oxide is apparent in the XPS data at the end of the runs, however; the only oxygen peak being that due to CO at 532.5 eV in the roomtemperature spectrum, whilst both the platinum–rhodium ratio and the accumulation of carbon are the same as found in a standard run. The activities of such pre-treated samples have been observed to be both slightly lower and slightly higher than found for a standard preparation but we attribute this inconsistency to the sample history and conclude that mild oxygen pretreatments have little effect (even transiently) on the HCN synthesis reaction kinetics over Pt-10%Rh.

# Discussion

To facilitate the discussion, we will begin by outlining our model for this reaction and then consider how the various results described above are consistent with this model.

A generalised reaction scheme for the three-component feed mixture is shown below.



Of the individual feed gases only  $NH_3$  exhibits a facile decomposition reaction, whereas any two reagents react readily as a binary mixture to give, principally, the products indicated. These initial products may, in turn, act as reagents for further conversion of components of the feed mixture (*e.g.* the reaction of NO and  $CH_4$ ), but there is little evidence in our data for such reactions playing a significant role.

The NH<sub>3</sub> oxidation reaction is particularly facile, with reaction being initiated under our experimental conditions at temperatures below 200 °C.<sup>17–19</sup> The product distribution for this reaction is controlled by the supply of surface oxygen and the surface temperature, with NO formation favoured over  $N_2$ formation at higher temperatures and higher  $O_2/NH_3$  ratios in the feed mixture.<sup>17-20</sup> When methane is added to the NH<sub>3</sub>-O<sub>2</sub> feed there is a stoichiometric deficit of oxygen and, once methane oxidation is initiated at higher temperatures, there is competition between NH<sub>3</sub> and CH<sub>4</sub> for the available oxygen; a knock-on effect of this will be an increase in the surface lifetime of NH<sub>x</sub> fragments. When CH<sub>x</sub> fragments generated by CH<sub>4</sub> activation are present on the surface at low concentrations, then they are readily scavenged by oxygen to yield the undesired combustion products CO and CO<sub>2</sub>. However, as the extent of methane activation increases, and consequently the surface  $CH_x$  population also increases, there are several effects. (i) The steady-state surface oxygen coverage will decrease; since adsorbed CH<sub>x</sub> species bind strongly to the Pt surface, thus blocking oxygen uptake, and the additional hydrogen present further enhances the reactive removal of oxygen. (ii) There is a corresponding reduction in the yields of both NO and CO<sub>x</sub>, whilst most of the oxygen is converted to  $H_2O_{r}$  (iii) The probability of reaction between  $NH_r$  and  $CH_r$ to give HCN (and H<sub>2</sub>) increases rapidly.

It follows from the above that efficient activation of  $CH_4$  is vital to HCN production. Indeed, we believe that the extent and nature of  $\overline{CH}_4$  activation is the single most crucial factor in obtaining high HCN yields, since this produces the high steady-state concentration of surface CH, species necessary to give HCN in high yield and selectivity. We assert that this is greatly facilitated by a specific state of the Pt surface, which can normally only be achieved by the presence of an oxygen component in the feed mixture when operating the catalyst at the nominal temperatures that we have employed. We further believe that this state corresponds to a particular type of surface structure involving Pt atoms of low coordination (or, conceivably, a certain degree of Pt atom mobility). Such a state would be expected to exhibit a very high surface free energy, but it could nevertheless be attained and sustained either by (i) the highly exothermic reactions of oxygen with surface hydrogen, nitrogen and carbon, or (ii) very high temperatures resulting from external heat input (as, for example,

in the Degussa process). The evidence from our work which supports the presence of surface restructuring and its role in generating atomic sites with low coordination during HCN synthesis is presented below, in the discussion of the separate sets of experiments, but we would note that the role of surface defects and coordinatively highly unsaturated metal atoms in the activation of alkanes on precious metal catalysts has also been emphasized by several other workers.<sup>21,22</sup>

In our standard runs, the catalyst surface just prior to initiation of reaction is either that produced by the standard cleaning procedure (of which an anneal in oxygen is an integral part) or that produced in a prior reaction run. The structure of both these surfaces is compatible with efficient methane activation or, at the very least, rapidly becomes so. As seen in Fig. 1 there is, therefore, a very brief period in which oxidation chemistry (especially NH<sub>3</sub> oxidation) predominates before the surface concentration of C fragments builds up to the level at which HCN synthesis occurs with concurrent generation of mainly the ammonia decomposition products (H<sub>2</sub>, N<sub>2</sub>) and water. At termination, there is again a brief period in which oxidation chemistry predominates as the sample rapidly cools. The CO generated in this process stabilises the 'dispersed' Pt which characterises the active surface; removal of this CO by heating in vacuum causes a collapse of this active surface structure such that the desorption process is essentially irreversible, as previously noted.

In the absence of oxygen, the initial HCN activity is quite high (since there are no competing oxidation reactions) but cannot be maintained at these temperatures (see, e.g. Fig. 4). The active surface sites are then either effectively removed by annealing or become decorated with inactive carbon deposits which are stable at these temperatures in the absence of oxygen. The remaining Pt terraces are essentially inactive for HCN synthesis or susceptible to deactivation by growth of unreactive (graphitic?) carbon overlayers. At the temperatures employed, the addition of  $CO_2$  to the feed and the consequent CO<sub>2</sub> decomposition does not yield a sufficiently high surface oxygen activity to prevent this deactivation occurring (Fig. 5). The fact that a reasonable HCN activity is transiently observed in the complete absence of oxygen also indicates that whilst surface oxygen species (O, OH) may facilitate CH<sub>4</sub> (and indeed NH<sub>3</sub>) activation by assisting the dissociative adsorption, the presence of such species is certainly not essential for methane conversion at these temperatures.

The results obtained following pretreatments of the Pt sample (Fig. 6) provide clear support for the proposed model of low coordination Pt atoms being most active in HCN synthesis. Ion bombardment leads to an enhanced initial HCN yield. Such an increase in yield might be attributable to a simple increase in the geometric area of platinum surface, but this is not consistent with the observation that the increase in yield is principally associated with an increase in selectivity to HCN. Instead, we attribute these effects to the artifical roughening of the surface induced by the high energy ion bombardment, i.e. to an increase in the concentration of low coordination sites which we have previously commented as being important to CH<sub>4</sub> activation. The subsequent gradual decline in yield (and selectivity) is then attributable to a gradual re-equilibration of the surface structure to that which is more stable under dynamic synthesis conditions, whilst the difference between the top two data curves in Fig. 6 illustrates once again how efficient vacuum annealing is in removing the surface roughening which leads to high HCN yields. It is also worth noting that the effects that we see with ion bombardment are very similar in many respects to those reported when Pt-monolith catalysts (and Pt-Rh gauzes) are transiently heated to higher temperatures in an oxygen rich mixture.<sup>23</sup>

Carbon deposition by pretreatment in pure ethylene is only partially effective in poisoning HCN synthesis. There is a very slight delay in the initiation of the reaction but the efficiency with which the catalyst regains most of its activity suggests that the carbon can be quickly (reactively) removed from particular sites to generate the necessary reactive surface centres. The remaining more stable carbon deposits have less effect on the catalytic reaction and their slow removal generates little in the way of further active surface.

The observed lag in the initiation of HCN synthesis after NH<sub>3</sub> pretreatment is, at first sight, inconsistent with the absence of any significant change in the surface composition. The effect is not, however, directly associated with the ammonia but with the effect on the surface structure of the extended annealing in a non-oxidising environment (since similar characteristics have since been seen after heating in an inert environment). We believe that this extended annealing destroys the nucleation sites at which CH<sub>4</sub> activation is initiated; i.e. the treatment has an opposite effect to that of ion bombardment, and a significant period of reaction involving exothermic oxidation processes (in which CO<sub>2</sub> and, especially, NO is produced) is required before the surface can restructure sufficiently to cause significant methane activation and thus build up the requisite concentration of surface CH<sub>x</sub> species for significant HCN synthesis to occur.

It is clear from the data presented in Fig. 3 and a comparison of the data of Tables 4-6 with those of Tables 1-3 that the addition of rhodium to the platinum is detrimental to HCN synthesis under our reaction conditions. More specifically, at a rhodium content of 10%, the HCN yield is substantially reduced, and the alloy surface is less than a third as active as platinum at an equivalent temperature. Owing to the limits of the apparatus, we were unable to test whether this reduction persists at temperatures higher than those investigated here; we note, however, that previous work on Pt-Rh alloys indicates that there is a significant increase in Pt surface segregation when such alloys are annealed in vacuum at temperatures above 1000 K<sup>24</sup> and, if the same segregation were to be observed under HCN synthesis conditions, then the difference in activity between pure Pt and the Pt-10%Rh alloy under commercial synthesis conditions might be less marked than we observe.

The further reduction in HCN activity seen after enrichment of the surface with Rh (by pretreatment in pure  $NH_3$  or reaction under anoxic conditions) indicates that the inhibiting effect of Rh is more pronounced still at higher surface concentrations. The driving force for this rhodium segregation on the alloy surface is thought to be the stabilisation of surface rhodium atoms by adsorbed hydrogen.<sup>25</sup> In this work, such a condition will clearly exist during both the anoxic runs and the catalytic decomposition of pure ammonia since ammonia readily decomposes to generate hydrogen which is less readily removed when oxygen is absent.

The rapid regeneration of HCN activity on Pt-10%Rh after pretreatment in ethylene suggests that the blocked sites on the alloy catalyst are more easily cleaned with oxygen than they are in pure platinum, which may have relevance to the resilience of such catalysts to the presence of higher hydrocarbons in the feedstock, but this needs much more investigation.

The key question which remains to be addressed is the cause of the reduced HCN activity in the presence of Rh. This could be attributed to the greater resistance of the alloy to the surface restructuring which we have proposed produces the high HCN yields on the pure Pt surface. In NH<sub>3</sub> oxidation, the greater resistance of the alloy to surface reconstruction has been demonstrated in a direct comparison of the rate of etching of Pt and Pt–10%Rh crystals placed in a high pressure reactor;<sup>26</sup> however, this does relate to conditions which are far more oxidising than those pertaining to HCN synthesis and could be associated with the volatility of higher oxidation state Pt compounds. At lower temperatures and in a less oxidising environment, a greater resistance to reconstruction might be related to the lower surface (and bulk) atom mobility

in the alloy that is to be predicted on the basis of its higher melting point and greater mechanical strength; certainly such a resistance to change is evident in our experiments by the way in which the sample history influences the results from the Pt-10%Rh alloy, which indicates that the surface equilibrates much more slowly to new reaction conditions than is the case for pure Pt. However, if differences in the observed extent of reconstruction were purely due to slower kinetics of reconstruction then the HCN activity of the alloy might ultimately more closely approach that of Pt, whereas the limiting value implied by the slow decline in activity that we see after pretreatment by ion bombardment suggests that this is definitely not the case; *i.e.* reduced restructuring under reaction conditions must be intrinsic to the nature of the alloy. Notably, Cowans et al.<sup>6</sup> also comment briefly on an apparent, inverse correlation between local Rh concentrations and the extent of localised surface restructuring in gauze catalysts used for HCN synthesis.

We have also observed an increase in oxidation catalysis on the Pt-10%Rh surface relative to that seen for pure Pt. Within our model this is a direct consequence of a less efficient activation of methane and would thus follow automatically if the alloy surface exhibits less reconstruction. However, it may also reflect the greater affinity of Rh for oxygen which will tend to increase the steady state concentration of surface oxidants and thus lead to enhanced yields of  $CO_x$  and NO at the expense of HCN selectivity.

Finally, we shall briefly consider how the results reported here may relate to features of the commercial Andrussow process. With regard to the comparison of Pt and Pt–10%Rh, our data indicates a clear benefit in using a pure Pt catalyst. This neglects any consideration of the mechanical benefits accruing from alloying but, nevertheless, our conclusion supports the observation of Hickman *et al.*<sup>27</sup> who, despite working under very different conditions, also noted that the addition of Rh reduces the HCN yield and selectivity.

The commercial process is characterised by substantial macroscopic restructuring of the gauzes and also by an induction period prior to optimal HCN production after the installation of new gauze packs; although unproven we believe these phenomena are related to the importance of microscopic surface restructuring that we have seen evidence for in this work.

# Conclusions

Studies of HCN synthesis on pure Pt and Pt-alloy surfaces, at total pressures of 0.02-0.15 Torr and temperatures of up to 780 °C, indicate that:

1. efficient methane activation is a crucial factor in obtaining HCN in high yield and with good selectivity,

2. the structure of the catalyst surface has a major influence on the reaction; in particular, low coordination Pt sites appear to be important in methane activation and HCN synthesis,

3. anoxic conditions do not give a sustainable HCN yield, suggesting surface oxygen atoms or exothermic oxidising reac-

4. a Pt-10%Rh alloy surface gives lower HCN yields and selectivity, and an increase in oxidation products when compared to pure Pt

5. reactions on the Pt-10%Rh alloy surface are further influenced by Rh surface segregation (under anoxic conditions) and memory effects (whereby the effects of previous sample treatments persist for some time under the testing conditions).

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