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The Formation of Isocyanic Acid (HNCO) by Reaction of NO, CO, and H_2 over Pt/SiO_2 and Its Hydrolysis on Alumina

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The reaction of mixtures of NO, CO, and H_2 over Pt/SiO_2 in combination with Al_2O_3 has been investigated with on-line Fourier transform infrared spectroscopy as the principal analytical method. With Pt/SiO_2 alone isocyanic acid (HNCO) can be observed directly as a substantial product. It comprises up to 45% of the CO converted in the temperature range from 200 to 300°C. The yield is maximized when the amounts of H_2 and CO in the input stream are equal. No HNCO can be observed in experiments in which Al_2O_3 is placed downstream of the Pt/SiO_2 or with a Pt/Al_2O_3 catalyst. Hydrolysis to NH_3 and CO_2 is then complete. For this reason it is unlikely that HNCO will escape a catalytic converter in vehicle use but it may be a significant intermediate during the warm-up phase. The formation of HNCO can be rationalized as resulting from the hydrogenation of NCO groups present in small concentrations on the Pt surface under conditions of high CO coverage. The yield of HNCO falls steeply above 300°C when the CO coverage is falling. It is unclear if hydrolysis of HNCO occurs by direct reaction of molecular HNCO on the Al_2O_3 surface or proceeds via the ubiquitous support-bound isocyanate species which have been observed in many previous studies. Previous observations of isocyanate formation in hydrogen-free systems can be rationalized as arising from HNCO formation by reverse spillover of hydrogen from OH groups on the support to generate HNCO on the platinum metal. This is then transported back to the support through the gas phase to form NCO groups. © 1996 Academic Press, Inc.

INTRODUCTION

The reduction of NO over platinum group metal catalysts is of great importance for removal of pollutants from vehicle exhausts (1–4). The usual reductants are CO and H_2, which occur typically at a ratio of 3 to 1 (1, 4), and hydrocarbons. Interestingly, hydrogen reacts with NO at temperatures as low as 70°C over supported platinum catalysts, but temperatures above 200°C are necessary with CO (5). Thus the hydrogen present in exhaust streams could, in principle, have a significant influence on the removal of NO at low temperatures.

The few studies with reaction mixtures containing all three of NO, CO, and H_2 (5–8) have shown NO reduction rates which were between those of the $NO + H_2$ and the $NO + CO$ systems, but much closer to the latter one. It is generally considered that reduction of NO by H_2 is inhibited by a strong adsorption of CO especially on platinum (5, 8–10). An implicit assumption has been that reactions in the NO, CO, and H_2 system are comprised solely of a superposition of those occurring in the $NO + CO$ and the $NO + H_2$ systems.

Recently, we observed that addition of H_2 to an equimolar mixture of $NO + CO$ not only increased the conversion of NO as expected, but it also multiplied the conversion of CO by up to 7 times (11, 12). This enhancement was apparent with Pt/Al_2O_3 and with Rh/Al_2O_3, but was more pronounced with the platinum catalyst. The major products were CO_2 and NH_3 and, especially with the rhodium catalyst, some N_2O. A net process with the stoichiometry

$$NO + CO + 1.5H_2 \rightarrow NH_3 + CO_2 \qquad [1]$$

seemed to account for 50–100% of all the CO_2 formed with Pt/Al_2O_3 and 20–50% with Rh/Al_2O_3. Two explanations seemed possible (11, 12). One was that oxygen atoms, produced by NO dissociation, reacted selectively with CO, the dominant surface species on Pt, while the corresponding nitrogen atoms were hydrogenated through to ammonia. An alternative was that an isocyanate intermediate, surface or gas phase, was involved and that hydrolysis of this material was the source of the near equal amounts of CO_2 and NH_3. The latter explanation seemed a possibility given the observations of Voorhoeve and Trimble (13–17) that various isocyanates comprised the major products of the reaction of NO, CO, and H_2 mixtures over most platinum group metals when they were in unsupported form.

In a recent short study (18) it has been shown that the second explanation is correct. Fourier transform infrared spectroscopy(FTIR) measurements revealed that isocyanic acid, HNCO, is a major product under steady state conditions if platinum is supported on SiO_2 rather than Al_2O_3. This paper describes the results of further studies of this system over a wider range of conditions.

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EXPERIMENTAL

The experimental procedures were similar to those described previously (11, 12, 18). The catalytic experiments were performed in a continuous flow tubular reactor made of silica (8 mm OD, 6 mm ID) operated at atmospheric pressure. Temperature was measured by a thermocouple located in a capillary (3 mm OD) within the reactor. The catalyst was placed concentrically between reactor wall and the capillary on top of a quartz wool plug. The Pt/SiO_2 catalyst was number 40–SiO_2–PtCl–L in the series prepared and characterized by Burwell *et al.* (19). 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 catalytic experiments were carried out with 75 mg samples ($\approx$0.2 cm^3 in volume) which were pretreated in a temperature programmed reduction (1% H_2/He, 9°C/min up to 350°C). This was followed by a 30-min equilibration with the standard CO and NO mixture at 350°C and slow cooling in the same mixture to reaction temperature. In some cases, 75 mg Al_2O_3 (Condea washcoat grade, surface area $\approx$140 m^2/g) was placed immediately below the Pt/SiO_2. Both samples were in the form of 108–180 μm particles formed by crushing, pressing, and sieving the original preparations.

The gas mixture was made up from four streams (UHP helium and three analyzed mixtures also in UHP helium) supplied by separate calibrated mass flow controllers to provide a total flow rate of 100 ml/min (STP). The standard concentrations of NO and CO were nominally 2000 ppm each. However, measurements at close to 100% conversion indicated that the actual NO inlet concentration was closer to 2200 ppm. The 10% difference reflects the limits of accuracy of the 1% NO/He mixture used.

Product analyses were performed on-line by mass spectrometry (MS) and by FTIR. After being sampled with the quadrupole mass spectrometer (Vacuum Generators model SX300), the gas stream flowed through a multiple pass cell (Infrared Analysis Inc., 2.4-m total pathlength) in the beam of a Mattson Cygnus 100 spectrometer fitted with an MCT detector. Spectra were acquired at 0.25 cm^{-1} resolution through the coaddition of 64 scans. The tubing (40 cm, 1/16″) from the reactor to the gas cell and the cell itself were maintained at approximately 100°C to prevent the formation and deposition of solid products such as NH_4OCN. Such phenomena were apparent in preliminary experiments using 4 m of connecting tubing at room temperature. The absorbances of individual lines of CO ($2103 + 2099$ cm^{-1}), NO (1875 cm^{-1}), N_2O (589 cm^{-1}), CO_2 (619 cm^{-1}), and NH_3 ($1102 + 1099$ cm^{-1}) were calibrated against diluted standard mixtures with the cell at the same temperature as that used in the catalytic experiments. Absorbances, and hence concentrations, were reproducible to a few percent. The MS data were used to determine the hydrogen concentration alone (by calibration against an accurately diluted 10.2% H_2/He standard). Concentrations of N_2 and H_2O were calculated from nitrogen and oxygen mass balances.

RESULTS

Figure 1a shows the FTIR spectrum of the product stream from the reaction of a mixture of NO and CO over Pt/SiO_2 at 230°C. The lines above 2300 cm^{-1} are due to the P-branch of the product CO_2 and those below 2230 cm^{-1} are due to the R-branch of the unreacted CO. The two underlying weak contours between 2260 and 2180 cm^{-1} with centers at 2225 cm^{-1} are due to the R- and P-branch lines of N_2O. The corresponding spectrum with 890 ppm of H_2 in the feed, Fig. 1b, shows an additional, broad unresolved pair of contours centered at 2269 cm^{-1}. There is also an increase in CO_2 concentration, and a decrease in CO concentration, and, much more noticeably now, the contour due to the P-branch lines of N_2O between 2225 cm^{-1} and 2180 cm^{-1}.

The new feature at 2269 cm^{-1} is shown in Fig. 1c as the difference spectrum of Fig. 1b less Fig. 1a. The overall structure

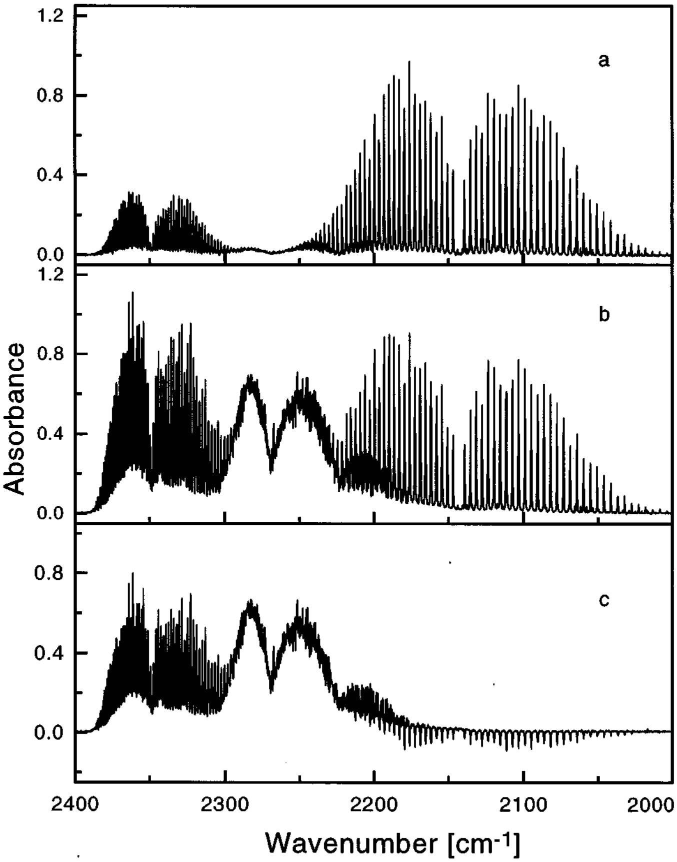

FIG. 1. Fourier transform IR spectra of the product stream from reaction at 230°C: (a) the reaction of 2000 ppm CO and 2200 ppm NO in helium over 75 mg of Pt/SiO_2; (b) as in (a) but with 890 ppm H_2 included in the feed; (c) the difference spectrum of (b)−(a).

matches that of pure HNCO as recorded by Herzberg and Reid (20). A recent study of the homogeneous reaction between hydrocarbons, NO and O_2, shows a practically identical spectrum (21), but one of much lower absorbance, which has also been attributed to HNCO.

A relationship between absorbance and HNCO concentration has been derived in two ways. Assuming that CO, CO_2, and HNCO are the only carbon-containing substances in the system, the difference between input CO and the sum of CO and CO_2 in the outlet is a measure of the HNCO made. Calculations using all suitable steady-state experiments from the present work indicated that the best average carbon balance could be obtained with [HNCO] = 240 ppm per absorbance unit at 2285 cm^{-1} (the peak of its R-branch contour). The corresponding extinction coefficient is 3.65×10^5 mole/cm (18). The spectrum of Herzberg and Reid (20), when translated to the 2.4-m cell used here, corresponds to ≈275 ppm per absorbance unit. The agreement between the two estimates is well within the likely accuracy of the measurements. The calculations in the subsequent sections use the value of 240 ppm per absorbance unit.

Figure 2 shows the results of a temperature programmed experiment (2°C/minute) with a feed containing H_2, CO, and NO. The maximum concentration of HNCO of 436 ppm is observed near 300°C and it decays sharply at higher temperatures. Hydrogen consumption is total above 240°C. Over the range from 220 to 260°C the level of HNCO lies between 120 and 200 ppm and the concentrations of CO_2 and NH_3 are close to equal. Above 260°C the CO_2 concentration continues to rise while the NH_3 concentration remains fairly constant. The concentration of N_2O parallels that of HNCO with a plateau from 220 to 260°C and a maximum only 10°C higher than that of HNCO.

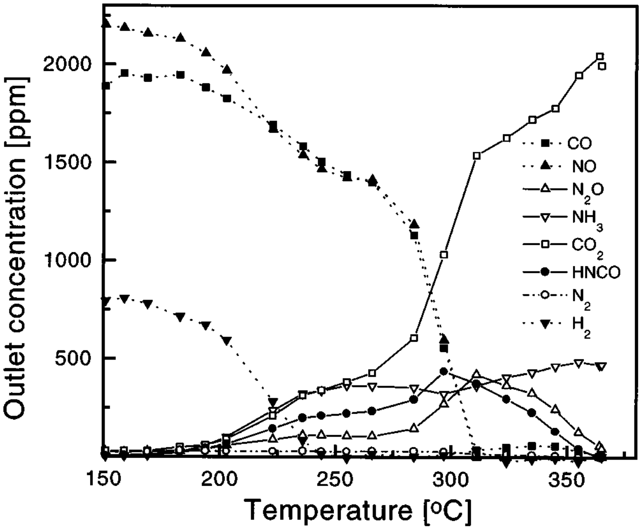

FIG. 2. Outlet concentrations versus temperature in a programmed experiment using a feed containing 2000 ppm CO, 2200 ppm NO, and 890 ppm H_2 over 75 mg of Pt/SiO_2.

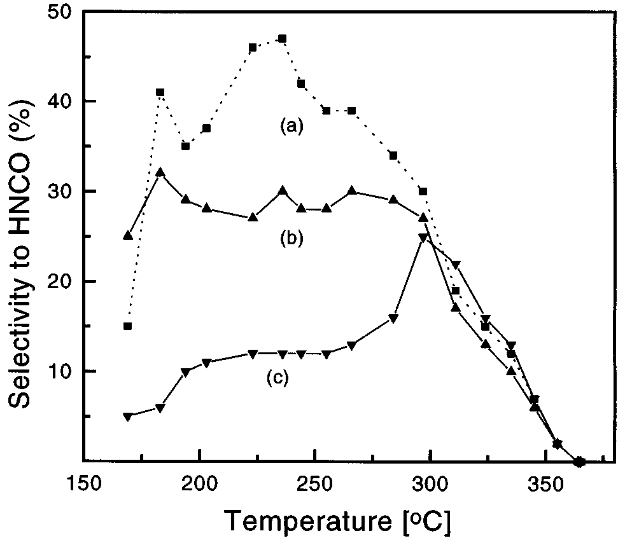

FIG. 3. Selectivity of HNCO formation for experiments of Fig. 2: (a) from CO calculated as HNCO/CO(reacted); (b) for the N atom in NO calculated as HNCO/NO(reacted); and (c) for H atoms calculated as HNCO/$2H_2$(reacted).

The selectivity with which the reactants formed HNCO rather than other products in the above experiments is shown in Fig. 3. At temperatures from 200 to 280°C it averages about 40% for CO (the balance is CO_2), 30% for the N atom of NO (balance ≈50% NH_3, ≈20% N_2O, and a little N_2), and 10 to 15% for H_2 (balance ≈60% NH_3 and 25% H_2O). There is an increase in the hydrogen selectivity at the temperature of maximum HNCO formation and steep declines in all selectivities above that as CO_2, N_2, and N_2O become the dominant products.

In previous experiments with Pt/Al_2O_3 at 230°C (12) it was shown that the conversion of NO and CO, and the production of CO_2 and NH_3, depended strongly on the concentration of H_2 present. Figure 4 shows the results of a repeat of those experiments using Pt/SiO_2 and with quantitation of HNCO as well. Each measurement was made after a steady-state was reached, which required 5 to 10 min, as reported previously (11). Consumption of hydrogen is nearly complete for inlet concentrations up to 900 ppm and in this regime the production of HNCO and NH_3, and the additional quantity of CO_2, is approximately proportional to the hydrogen consumption. With increasing amounts of emergent hydrogen, production of HNCO, CO_2, and N_2O tends to plateau while that of ammonia continues to increase. The latter increase is likely to be due to the NO + H_2 reaction since the enhancement of the NO conversion then exceeds that of CO by a large amount.

Formation of HNCO also occurred in experiments where the sum of CO + H_2 was kept constant at 2000 ppm while their ratio was varied (Fig. 5). The maximum concentration of 220 ppm occurred when the inlet concentrations of CO and H_2 were equal which also coincided with the maximum

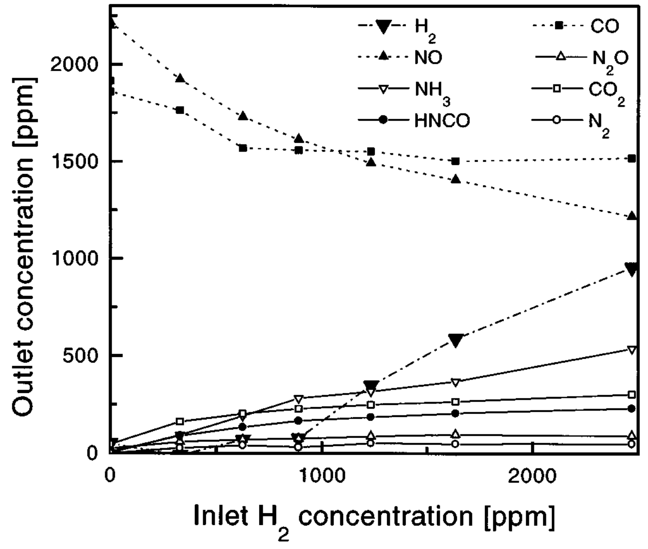

FIG. 4. Outlet concentrations as a function of inlet hydrogen concentration in experiments using 2000 ppm CO and 2200 ppm NO over 75 mg of Pt/SiO_2 at 230°C.

of NH_3 and CO_2 formation. Somewhat surprisingly, no NH_3 was detected with the feed containing only NO and H_2. Subsequent experiments feeding only NH_3 and NO showed a fast reduction of NO by NH_3. Hence it is quite possible that ammonia was formed initially but immediately reacted further. Of special interest is a reaction with a CO-to-H_2 ratio of 3 : 1 which is typical of that found in car exhaust (4). The concentration of HNCO is 140 ppm and the selectivities to it are similar to those given in Fig. 3, i.e., 40% for CO and 30% for the N atom of NO.

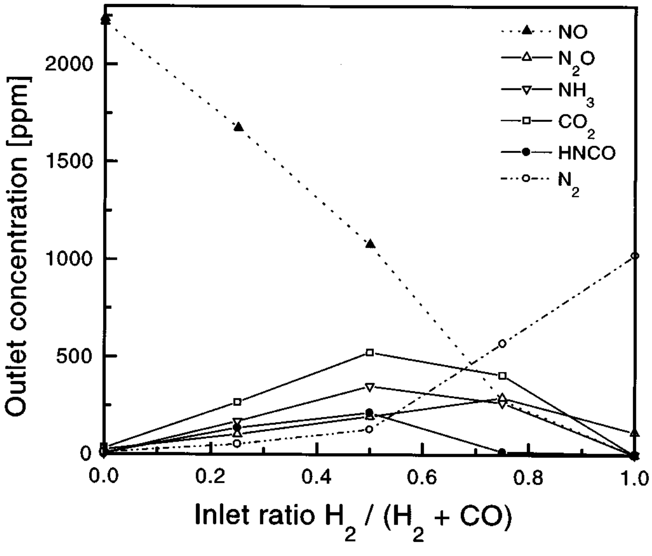

FIG. 5. Outlet concentrations as a function of the feed H_2-to-$H_2 + CO$ ratio with $H_2 + CO = 2000$ ppm in experiments using 2200 ppm NO over 75 mg of Pt/SiO_2 at 230°C.

The results so far have demonstrated the formation of HNCO beyond any doubt. The amount is substantial, with up to 45% of the CO converted found in HNCO. Further experiments were carried out to see if HNCO undergoes reaction on Al_2O_3, the most commonly used support in emission control catalysts. An amount of Al_2O_3 equivalent to the catalyst (75 mg) was placed immediately behind the Pt/SiO_2. Figure 6 shows the spectrum of the product stream using the Pt/SiO_2-plus-Al_2O_3 combination in comparison with that for Pt/SiO_2 alone. The addition of Al_2O_3 leads to the total disappearance of HNCO, as is evident by the absence of its characteristic P and R branch contours at 2245 and 2285 cm^{-1} in Fig. 6b. The maximum concentration of residual HNCO is at most 10 ppm (absorbance <0.04) and almost certainly less than 2 ppm (absorbance <0.01). The difference spectrum, Fig. 6c, shows the disappearance of HNCO as a negative peak. The positive peaks for CO_2 (2300 to 2400 cm^{-1} and, less obviously, for NH_3 (below 1200 cm^{-1}) indicate formation of these species by reaction of the HNCO. The concentrations of CO and NO are unaffected by the presence of the Al_2O_3 as indicated

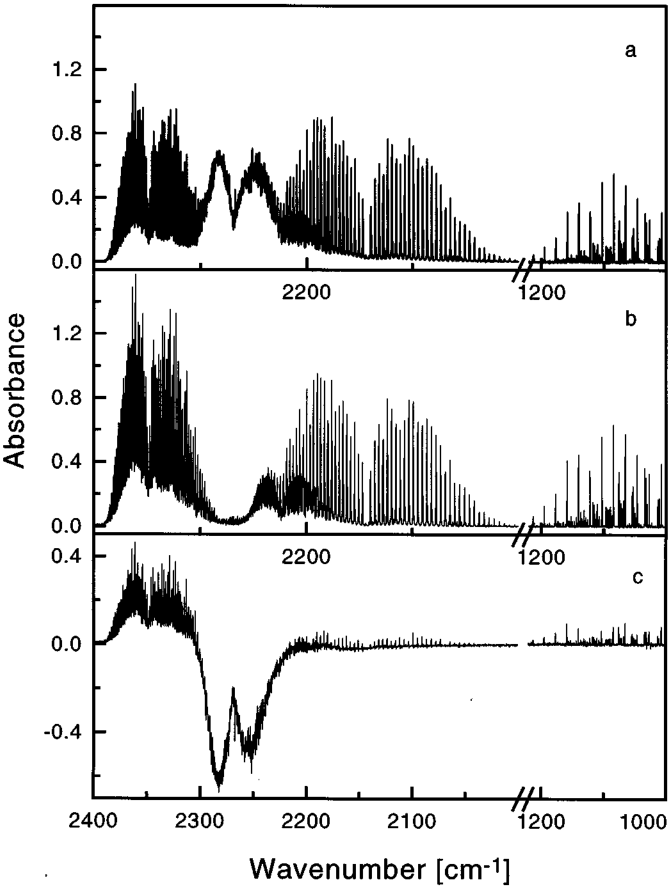

FIG. 6. Fourier transform IR spectra of the product stream from reaction of 2000 ppm CO, 2200 ppm NO, and 890 ppm H_2 at 230°C: (a) using 75 mg of Pt/SiO_2 alone; (b) using 75 mg Pt/SiO_2 followed by 75 mg of Al_2O_3; a (c) the difference spectrum of (b)−(a).

by the absence of lines due to CO (and also due to NO, although these are not shown) in the difference spectrum.

The experiments of Figs. 4 and 5 were repeated with Al_2O_3 downstream, and no HNCO was found under any conditions. Again, the conversions of CO and NO were similar in the experiments with and without Al_2O_3. Figure 7 shows the differences in concentration between the pair of experiments carried out under the conditions of Fig. 4 but include measurements made with higher H_2 concentrations. The negative values of HNCO indicate that up to 280 ppm was present when using Pt/SiO_2 alone but not with $Pt/SiO_2 + Al_2O_3$. The positive values for NH_3 and CO_2 of 200 to 300 ppm correspond well to that expected for the conversion of the HNCO which has been lost through hydrolysis on the Al_2O_3. It should be noted here that these experiments were run on different days with H_2 concentrations set in random order and with exit NO and CO concentrations above 1000 ppm. The fluctuations evident for the latter compounds in Fig. 7 reflect errors that are inescapable when subtracting sharp lines with high absorbance. The same general behavior was displayed in the pair of experiments using a constant sum of $CO + H_2$ concentrations in the region where the H_2 fraction was ≤ 0.5. The observed values for CO_2 and NH_3 were 100–200 ppm with equivalent negative values for HNCO. The scatter in the data was too great to allow meaningful conclusions once the fraction of H_2 in the input stream exceeded 0.75.

Additional experiments were performed with the same 1 wt% Pt/Al_2O_3 catalyst used previously (11, 12). Again, no HNCO was found in the product stream from the reactor. The results were very similar to that obtained with the combination of Pt/SiO_2 followed by Al_2O_3.

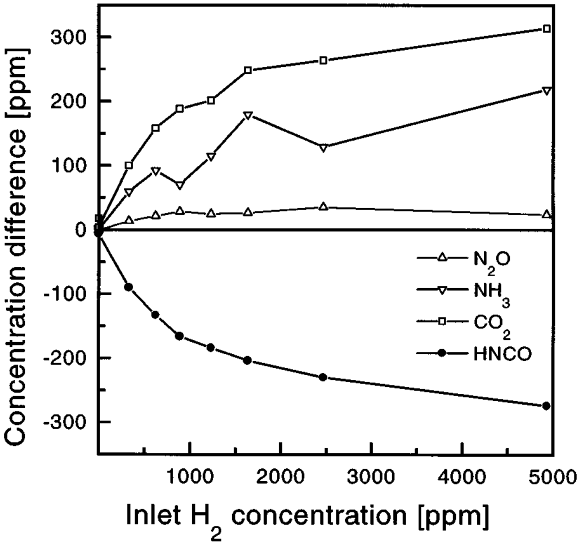

FIG. 7. Concentration differences (values for experiments using 75 mg Pt/SiO_2 followed by 75 mg Al_2O_3 less those when using 75 mg Pt/SiO_2 alone) as a function of the inlet hydrogen concentration when using 2000 ppm CO and 2200 ppm NO at 230°C.

DISCUSSION

General. The present work confirms and clarifies our earlier findings of the positive effect of H_2 on the conversions of NO and CO (11), the proposed formation of an HNCO intermediate (12), and the subsequent detection of HNCO as a substantial product over silica supported platinum (18). The only previous reports of HNCO from such mixtures are those of Voorhoeve and Trimble (14, 16) for unsupported palladium and iridium sponges. The corresponding platinum catalyst gave predominantly ammonium cyanate, NH_4OCN, instead (13, 15). The reason for the result differing from that found here for Pt/SiO_2 is unclear but one possibility is that the NH_4OCN observed by Voorhoeve and Trimble (13, 15) was produced by the combination of HNCO and NH_3 in cool regions downstream of their reactor. In the present work HNCO was not observable in preliminary experiments with the infrared cell and its connecting tubing left unheated. This could have been due to deposition of solid products on the interior walls of the tubing but no analyses were attempted.

The formation of HNCO on Pt/SiO_2 may be represented by the net reaction

$$CO + NO + 1.5H_2 \rightarrow HNCO + H_2O \qquad [2]$$

occurring on the metal. The apparent activation energy for this reaction is ≈88 kJ/mol as estimated from the low temperature data in Fig. 2. Addition of Al_2O_3 downstream caused the disappearance of HNCO and the formation of corresponding amounts of NH_3 and CO_2. Obviously, HNCO hydrolyzes on Al_2O_3 to form the products

$$HNCO + H_2O \rightarrow NH_3 + CO_2. \qquad [3]$$

The hydrolysis on Al_2O_3 must be very fast which agrees with the fact that support-bound NCO species hydrolyze even at room temperature (22–25). The observable net reaction on alumina-supported metal catalysts would then be the addition of [2] and [3], i.e., reaction [1], which indeed represented much of the net reaction with Pt/Al_2O_3, and to a lesser extent with Rh/Al_2O_3, when hydrogen was present (12).

It is possible that some HNCO hydrolysis takes place on the SiO_2 support when using the Pt/SiO_2. Indeed, the formation of CO_2 and NH_3 in similar amounts at temperatures from 220 to 260°C, Fig. 2, could indicate that the bulk of these products arises by this process rather than by other steps on the metal. The near absence of NH_3 with unsupported platinum could support this idea, but the formation of the NH_3 necessary to produce the NH_4OCN observed in those experiments (13, 15) is then uncertain.

Reactions on the platinum metal. Isocyanic acid is almost certainly formed on the metal surface by reaction of H_2, NO, and CO. That means that reaction steps leading to HNCO must be more favorable than competitive reactions or, in other words, the presence of hydrogen must open a faster reaction path. A result is the observed positive effect of hydrogen on the conversions of NO and CO as reported previously. Several explanations are possible depending on the identity of the rate determining step. The rate of NO dissociation, if slow, could be increased by "hydrogen-assisted" NO dissociation (26, 27), as discussed before (11, 12):

$$^*NO + H^* \rightarrow N^* + {}^*OH \qquad * = \text{surface Pt atom.} \quad [4]$$

Other mechanisms to facilitate NO dissociation, e.g., decreased CO coverage, division of inhibiting CO islands, or increased electron density by adsorbed hydrogen, may be considered but Eq. [4] is preferred because it would lead naturally to the formation of water (from the OH species) as required for the hydrolysis step [3].

Another possible slow step is removal of adsorbed nitrogen atoms. The formation of HNCO suggests an initial equilibration reaction to form NCO [5] and desorption in the presence of hydrogen via [6]

$$N^* + {}^*CO \rightleftarrows {}^*NCO + * \quad [5]$$

$$^*NCO + H^* \rightarrow HNCO(gas) + 2*. \quad [6]$$

Adsorbed NCO species on Pt decompose at 310–330 K to adsorbed N and CO (28, 29) and have usually been discounted as potential reaction intermediates although this view has been the subject of some revision (30, 31). However, under actual reaction conditions at <300°C the coverage of CO is very high and a different situation may prevail. If the above equilibrium is shifted to the right then small amounts of NCO could still be present on the Pt surface. Adsorbed hydrogen could then lead to the irreversible desorption of HNCO and the continuous formation of Pt-bound NCO via reaction [5]. It is highly significant that HNCO formation declines steeply above 300°C (Fig. 2). It is in this region that CO coverage falls and a sharply lower probability of forming HNCO is to be anticipated.

While the pathway via HNCO may be favored by high CO coverages and temperatures <300°C, other routes such as the pairing of nitrogen atoms,

$$N^* + N^* \rightarrow N_2(gas) + 2*, \quad [7]$$

and/or the formation and decomposition of N_2O as envisaged by Cho (32) for the NO + CO reaction on rhodium,

$$N^* + NO^* \rightarrow N_2O(gas) + 2* \quad [8]$$

$$N_2O(gas) + * \rightarrow {}^*N_2O \rightarrow N_2(gas) + O^*, \quad [9]$$

will be inhibited. The reaction to form ammonia,

$$N^* + 3H^* \rightarrow {}^*NH + 2H^* + * \rightarrow {}^*NH_2 + H^* + 2* \rightarrow NH_3(gas) + 4*, \quad [10]$$

may also be less likely than competitive HNCO formation [6], since the latter reaction requires only one hydrogen atom rather than the three necessary for [10]. However, the alternative routes for N atom removal, [7, 8, and 10], will be enhanced as CO coverages fall above 300°C. The data in Fig. 2 show the expected transition in product distribution.

In summary, it appears quite likely that the positive influence of hydrogen on NO and CO conversions stems from the introduction of an additional reaction path through HNCO desorption. Adsorbed NCO and HNCO are thus identified as important reaction intermediates.

The previous work with Pt/Al_2O_3 discussed the possibility that CO_2 and NH_3, the predominant products then observed, might arise because oxygen atoms formed by dissociation of NO reacted preferentially with adsorbed CO rather than with adsorbed H because of the high coverage of CO (11, 12). A contribution by this reaction cannot be entirely ruled out with either Pt/Al_2O_3 or Pt/SiO_2. However, the quantity of HNCO detected with Pt/SiO_2 implies that at least 45% of the CO_2 formed with the alumina-based catalyst could arise via the formation and hydrolysis of HNCO. A corollary of this interpretation is that it is possible that ammonia formation, which is more pronounced with Pt and Pd than with Rh or Ru (4, 5, 7, 8), reflects the relative propensity of the metals for HNCO formation. The lesser tendency of rhodium to give ammonia can be attributed to a lower concentration of CO on its surface and hence a reduced driving force for reactions [5] and [6]. Our previous results show that hydrogen does increase the rate of the NO + CO reaction for Rh/Al_2O_3 (12) but the effect is less than with Pt/Al_2O_3 and the quantity of nitrogen fixed as N_2O is greater than that fixed as NH_3.

Role of the support. Clearly, HNCO hydrolyses on Al_2O_3 to form NH_3 and CO_2 as shown by the experiments with pure Al_2O_3 downstream of the Pt/SiO_2. The mechanism of hydrolysis is quite uncertain but two cases may be differentiated. First, one might suspect hydrolysis to occur in a rapid reaction on the Al_2O_3 surface without prior formation of chemisorbed intermediates, possibly via carbamic acid,

$$HNCO + H_2O \rightarrow (H_2NCOOH) \rightarrow NH_3 + CO_2, \quad [11]$$

as was suggested by Unland (23).

The alternative is that HNCO hydrolysis proceeds via the isocyanate species (NCO) adsorbed on Al_2O_3 which have been reported in numerous studies of alumina-supported metals (22, 23, 25, 31, 33–39), but are generally regarded as spectator species (31). Such groups are known to be readily hydrolyzed even at room temperature so that at least part of the additional CO_2 and NH_3 observed when Al_2O_3 is present could arise via the net process

$$NCO^- + 2H_2O(ads) \rightarrow NH_3(gas) + CO_2(gas) + OH^-. \quad [12]$$

Both possibilities, reaction [11] and reactions [12], result in the formation of ammonia and carbon dioxide. The difference is that in the former case NCO groups bound to the alumina would be purely spectator species, while in the alternate these NCO groups are a necessary part of the chain. The latter path would demand a rethinking of the role of support-bound NCO groups in car exhaust catalysis.

Spillover of NCO and the role of HNCO in other systems. Support-bound NCO species have been reported in many publications in which only NO and CO were used (22–25, 31, 33–40). Generally, NCO was thought to be formed on the metal but then spilled over to the support (3, 22, 28, 30, 35) by an "immeasurably fast process" (39). Indeed, the spillover process must be very fast as NCO consumption and accumulation occurred when water was introduced or removed as step changes (11). The amount of NCO involved was eight times the number of metal atoms. The question arises as to how spillover and surface diffusion of NCO, a three-atom species, could possibly be so fast.

Transport of NCO as HNCO, formed on the metal as described above, via the gas phase seems a viable explanation in the presence of hydrogen but at first glance is seemingly unlikely when using CO and NO alone. However, hydroxyl groups are one possible source of hydrogen. It has been observed on supported metal catalysts that support-bound OH groups react with CO to form CO_2 and H_2 (41–44). This requires reverse spillover of hydrogen from the support to the metal where the reaction occurs.

The same process could occur in the presence of CO and NO but with HNCO being formed on the metal

$$\text{H(ex support OH groups)} + {}^*\text{NCO(metal)} \rightarrow \text{HNCO(gas)}. \qquad [13]$$

The HNCO is subsequently transported via the gas phase and deposited elsewhere as support bound NCO groups.

$$\text{HNCO(gas)} + \text{O}^{2-} \rightarrow \text{NCO}^- + \text{OH}^-. \qquad [14]$$

This is consistent with the results of Lorimer and Bell (24) who observed the formation of Si–NCO groups on a SiO_2 reference disc, remote from a Pt/SiO_2 catalyst disc, in an atmosphere of NO and CO, and suggested HNCO formation using hydroxyl groups and long-range transport as a possible explanation. The reverse spillover of hydrogen would be expected to be fast on supports with a high initial concentration of OH groups and a fast diffusion rate of hydrogen atoms. Martin and Duprez (45) measured the diffusion processes on different supports at 400°C and found that the concentration of OH groups on Al_2O_3 is 15 times that on SiO_2, while the diffusion rate of H is twice as great. Indeed, formation of NCO is much faster, and the observed infrared bands are more intense, with alumina-supported catalysts than with the corresponding silica ones (22). Thus the proposed path via reverse hydrogen spillover and formation of HNCO offers a possible explanation for the formation of support NCO.

Further support for HNCO transport is found by reexamining some deactivation phenomena. Decline of activity has been correlated to the buildup of support-bound NCO species (24, 37) leading to the conclusion that NCO cannot be a reaction intermediate in the CO + NO reaction. However, the findings presented here offer a different interpretation. Hydrogen is found to enhance activity. Even when it is not present the activity might be higher as long as hydrogen from OH groups can spill over to the metal. HNCO may be formed but only as an intermediary because it reacts with other OH groups to form NH_3 and CO_2 and some NCO species. Eventually all OH groups are consumed, the activity decreases, and NCO accumulates on the support without being able to react further with OH or H_2O. Thus, it is the loss of surface OH groups which causes the deactivation rather than the observed increase in the number of NCO groups. Interestingly, the activity is restored upon addition of water (37), which is in accordance with this scenario.

Findings with other systems also fit the above picture. Paul *et al.* (46) studied the reaction between ammonia and carbon monoxide over Pd/SiO_2 and found spillover of NCO only when a H-containing species was present. In this case HNCO was detected as a gaseous intermediate. Of course, hydrogen is needed if NCO can migrate only via HNCO. In another study Pd black and TiO_2 were mechanically mixed (47). Support-bound isocyanates were detected only after hydrogen treatment, and accordingly spillover was thought to proceed via a newly formed metal/intermetallic phase. Again, formation of HNCO by adsorbed hydrogen and subsequent transport via the gas phase seems more likely.

CONCLUSIONS

Isocyanic acid is an important product of the reaction of NO with CO in the presence of H_2 on a Pt/SiO_2 catalyst. The same product is not seen with Pt/Al_2O_3 due to a rapid hydrolysis of HNCO on the alumina. It is possible that HNCO plays a more significant role in the chemistry of emission control catalysis than has been previously realised. Formation of the support-bound isocyanate species observed in hydrogen-free systems may also involve HNCO, formed from OH groups by reverse spillover, as a gaseous transfer agent.

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