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Conversion of NO to Isocyanic Acid and Ammonium Cyanate over Pd, Ir, and Pt–10% Rh Catalysts

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The formation of HNCO and NH_4OCN was studied over unsupported Pd, Ir, and Pt–10% Rh catalysts. The reactions studied are $2NO + 3CO + 2H_2 \rightarrow NH_4OCN + 2CO_2$, $2NO + 4CO + H_2 \rightarrow 2HNCO + 2CO_2$, and $2NO + 2NH_3 + 4CO + H_2 \rightarrow 2NH_4OCN + 2CO_2$. The yields of NH_4OCN in the first reaction were 97% for the Pt–10% Rh catalyst. The best yield of HNCO in the second reaction was 75% over the Ir catalyst, with an additional 22% of the NO reacting according to the first reaction, for an overall NO → NCO conversion of 86%. The third reaction was carried out with a yield of 86% over Pt–10% Rh. These reactions may be attractive synthetic routes to ammonium cyanate, or its isomer urea, and to isocyanic acid or its trimer isocyanuric acid. The effects of H_2O and H_2 in the inlet gas of the reaction were found to depend on the temperature and on the H_2O/H_2 ratio. The results were explained by a reaction scheme which places central importance on the adsorbed NCO intermediates. Hydrogenation and hydrolysis of NCO are shown to lead to HNCO and NH_3. It is argued that the mechanistic reaction scheme presented accounts for the observed product distributions for Pt, Rh, Ru, Os, and Cu–Ni in addition to Pd, Ir, and Pt–10% Rh.

The formation of (iso)-cyanate surface intermediates in the reaction of NO with CO is well established for a variety of supported catalysts, including Pd/Al_2O_3 (*1*, *2*), Ir/Al_2O_3 (*1*), Pt/Al_2O_3 (*1*, *3–5*), and Rh/Al_2O_3 (*1*). Recently, it was discovered that the reduction of NO with CO and H_2 may be used to synthesize NH_4OCN with nearly quantitative yields (Eq. (1)), using unsupported Pt or Rh as catalysts (*6*, *7*):

$$2NO + 3CO + 2H_2 \rightarrow NH_4OCN + 2CO_2. \quad (1)$$

In contrast, HNCO was found to be the main product in the reduction of NO with CO and H_2 over unsupported Pd and Ir catalysts (Eq. (2)), along with some production of NH_4OCN (*8*, *9*):

$$2NO + 4CO + H_2 \rightarrow 2HNCO + 2CO_2. \quad (2)$$

These processes may be interesting in their own right as manufacturing routes to HNCO, NH_4OCN, and their derivatives (*6*, *8*). They also firmly establish the importance of NCO surface intermediates in the interaction of NO, CO, and H_2 at metal surfaces. The present work extends the earlier studies of these processes for two reasons. First, we attempt to obtain more insight into the surface chemistry of these systems by studying the dependence of the rate of formation of HNCO and NH_4OCN on the residence time in the catalyst volume and on the composition

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of the gas phase. Second, the mechanisms proposed for the formation of NH_4OCN and HNCO lead to certain predictions which we wanted to pursue. The main one was that a process such as

$$2NO + 2NH_3 + 4CO + H_2 \rightarrow 2NH_4OCN + 2CO_2 \quad (3)$$

should be possible on catalysts such as Pt or Rh which, in the absence of NH_3 in the feed, lead to conversion of NO to NH_4OCN according to Eq. (1). The economically attractive difference between Eqs. (1) and (3) is, of course, that twice as much NH_4OCN is produced per mole

TABLE 1

Catalysts Used in Reduction of NO with CO and H_2

Name	Composition	Preparation	Surface area (m^2/g)
Pd	99.999%	United Mineral and Chemical Corp. (lot 34515)	0.40
Ir	99.95%	Engelhard Industries, Newark, N.J.	0.58
Pt–Rh	90% Pt, 10% Rh; Al 0.5–0.9%; 0.0x% Sb, Pd, and Ir; 0.00x% Mn, Pb, Fe, and Ag[a]	Alloy Surfaces Co., Inc., Wilmington, Del.; gauze, 100-μm wire gauge, treated by proprietary process (*13*)	6.0

[a] Semiquantitative spectrographic analysis by Fairfield Testing Laboratories, Fairfield, N.J.

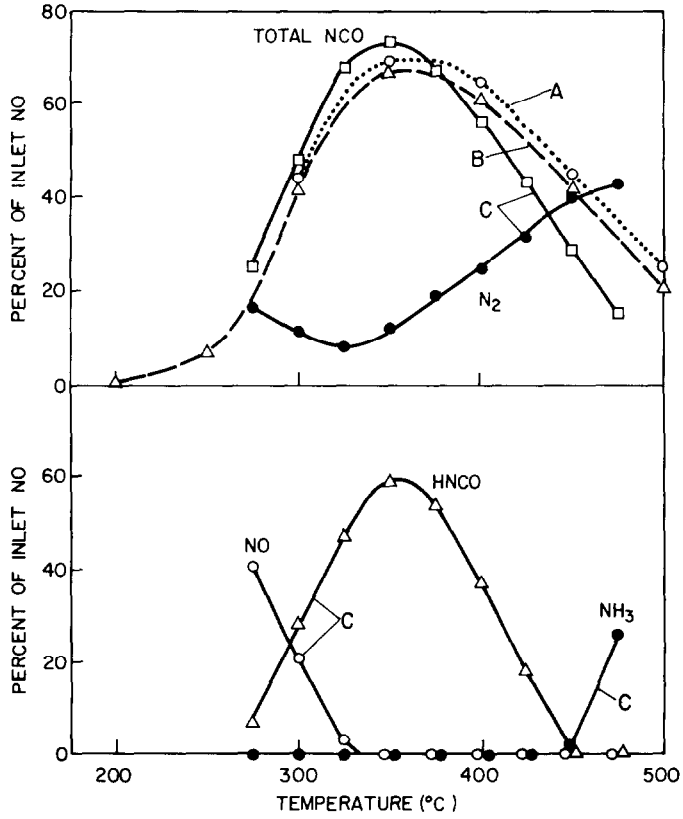

FIG. 1. Conversion of NO to NCO (total, in HNCO and NH_4OCN), N_2, NO, and NH_3 (total, in NH_3 and NH_4OCN). Pd catalyst. Conversion is plotted as percentage of N in inlet NO recovered as NCO, N_2, and NH_3. (A) Pd reduced in pure H_2 for 2 hr at 450°C; (B) same after 16 hr at room temperature in flowing pure He; (C) same after extensive reduction at 500°C. Gas mixture is 0.3% NO, 0.5% H_2, 5% CO in He at a flow rate of 4×10^4 ml/hr/m^2 of Pd in the sample.

of NO converted. In Eq. (3) all NO is apparently converted to NCO, whereas in Eq. (1) half is converted to NH_3.

EXPERIMENTAL METHODS

All experimental methods employed were identical to those reported previously. Mixtures of NO, CO, H_2, and H_2O diluted with He are passed over 1 to 3 g of the catalyst contained in a quartz fixed-bed reactor. The effluent from the reaction is split. One part is analyzed by gas chromatography for NO, N_2, CO, and H_2 (*10*). One part is analyzed for cyanate by absorption of the latter in an alcoholic solution of ammonium acetate, conversion of cyanate into urea, and colorimetric measurement of the urea (*11*). Analysis for HCN has been performed by opto-acoustic detection in the gas phase (*12*). From the analyses for NO, N_2, and total cyanate, the formation of NH_3 is calculated. At low temperatures, a small amount of N_2O, which is here neglected, may be found. The catalysts used are listed in Table 1. The Pt–10% Rh catalyst had been treated by the manufacturer to provide high surface area and activity (*13*).

RESULTS

Palladium

To obtain an optimum yield of HNCO over Pd, it was necessary to prereduce Pd. An effective procedure (*9*) was to pass pure H_2 over the catalyst at room temperature for several hours (accompanied by uptake of H_2 in the bulk of Pd), followed

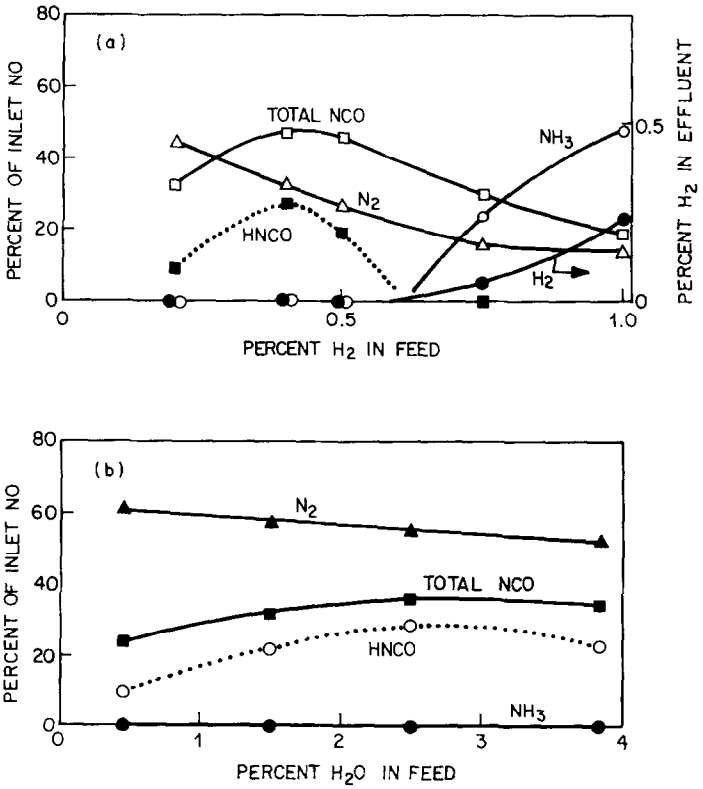

FIG. 2. Effects of H_2 and H_2O on the conversion of NO over Pd at 425°C. Reduced Pd catalyst. Flow rate, 4×10^4 ml/hr/m² of Pd in the sample. Gas mixture includes 0.3% NO and 5% CO in addition to the H_2 or H_2O specified. (a) Effect of H_2 at 0% H_2O. (b) Effect of H_2O at 0% H_2.

TABLE 2

Effect of H_2 and H_2O Concentrations on the Formation of NCO Compounds over Palladium

Temperature (°C)	Flow rate (ml/m²·hr)	Inlet gas[a]		Yield[b]		Conversion of NO (%)
		% H_2	% H_2O	% N_2	% NCO	
350	4×10^4	0.5	0	11.5	72.5	100
350	4×10^4	0.5	3.4	10	75.5	100
350	3.5×10^4	0	3.4	39	38	87
350	3.5×10^4	0	0.2	34	20	80
350	3.5×10^4	0.2	0.2	22	54.5	94.5
500	4×10^4	0.5	0	NM	21	100
500	4×10^4	1.0	0	NM	1.5	100

[a] The balance of the inlet gas was 0.3% NO, 5% CO, and He.
[b] Yields calculated on the basis of moles of NO converted into NCO or N_2. NM, not measured.

by reduction in flowing pure H_2 at 450 to 500°C. Figure 1 shows the variations of the total yield of NCO (as HNCO and NH_4OCN) with temperature for various prereduction procedures. The maximum NCO yield of 73% in curve C of Fig. 1 corresponds to 60% conversion of NO to HNCO and 28% to NH_4OCN (*8*). Figure 2 shows two series of experiments with Pd at 425°C, which is in the range of temperatures where the hydrogenation of surface cyanate species was proposed to be important in the formation of NH_3 (*7*, *8*). In Fig. 2a, the concentration of H_2 was varied from 0 to 1.0% in the absence of H_2O in the feed gas mixture. The total NCO yield comprised of HNCO + NH_4OCN first rises with increasing H_2 concentration, and then declines after reaching a maximum at 0.4% H_2. The decline is accompanied by a

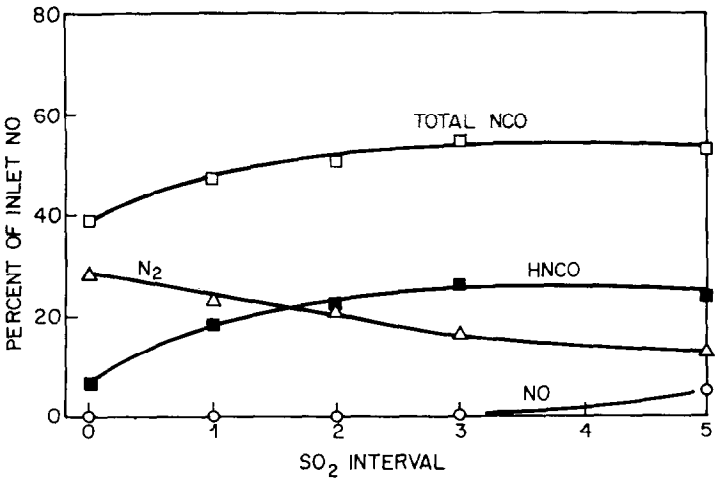

FIG. 3. Improvement of selectivity for cyanates by dosing Pd with SO_2. Temperature, 450°C. Flow of 0.3% NO, 0.5% H_2, and 5% CO in He at a rate of 4×10^4 ml/hr/m² of Pd surface in the sample. Each dose corresponds to a 5-min admission of 5 ppm of SO_2 to the gas. Measurements taken after the SO_2 has been purged from the gas phase.

sharp rise of the formation of NH_3. At 500°C, the effect of adding H_2 beyond the optimum amount was a sharp decrease in the yield of NCO (Table 2). In Fig. 2b, the concentration of H_2O was varied in the absence of H_2. Increase of the H_2O concentration does not increase the yield of NH_3 at this temperature (425°C) but does increase the yield of NCO by increasing the desorption rate of HNCO, perhaps by a reaction such as

$$NCO^- + H_2O \rightarrow HNCO + OH^- \quad (4)$$

or through prior formation of H_2 via the

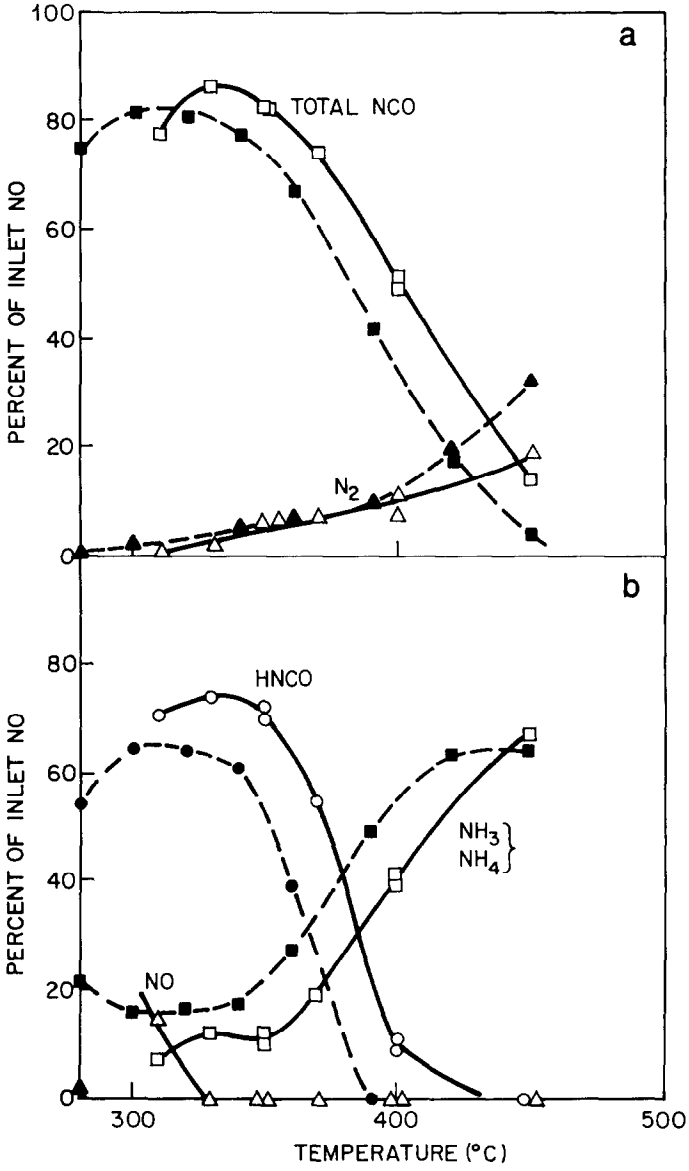

FIG. 4. Conversion of NO to NCO (total, in HNCO and NH_4OCN), N_2, and NH_3 (total, in NH_3 and NH_4OCN). Ir catalyst. Conversion plotted as percentage of N in inlet NO recovered as NCO, N_2, NO, and NH_3. Solid lines: Ir reduced in flowing H_2/He (80:20) at 450°C, 100 min. Dashed lines: Ir as received. Panels a and b separated for clarity.

water–gas shift reaction. There is no evidence for the hydrolysis of NCO at this temperature. At 350°C, hydrogenation of NCO to HNCO and NH_4OCN competes with hydrolysis of NCO and coupling to N_2. Table 2 shows that only in the absence of H_2 does surface NCO enter into the competing reactions. At 350 and 400°C, the effect of the flow rate was studied for a gas mixture of 0.3% NO, 0.5% H_2, and 5% CO in He. The total yield of cyanate compounds (HNCO and NH_4OCN) was independent of the flow rate, remaining at 72% for 350°C and 63% at 400°C. At 350°C one is close to the maximum in the NCO yield and to the point where NO has just been completely converted. The insensitivity of the yield to the flow rate in that temperature range is similar to the experience with Pt (*7*) and is thought to reflect the compensating effects of the changing nature of the surface (from reduced to oxidized as the higher flow rate allows a larger fraction of NO to remain) and the time dependence of the hydrolysis reaction. At 400°C over Pd, desorption of HNCO and hydrogenation of NCO to NH_3 appear to have comparable rates. Quantitative modeling of the reactions is necessary to verify these qualitative reasonings.

In the case of Pt (*7*), hydrogenation of NH_4OCN was distinguishable as a consecutive reaction at about 430°C, but not at 410°C and lower. Figure 2 suggests that Pd may behave in a similar way at 425°C and above. The hydrogenation (or reduction) activity may be "poisoned" by dosing the Pd with SO_2. Figure 3 shows that at 450°C this results in an improved selectivity for HNCO and total NCO.

Iridium

The catalytic activity of Ir for the reduction of NO to HNCO is not very dependent on the prereduction of the catalyst, although some effect was noticed (Fig. 4). For the catalyst which was prereduced at 450°C in H_2, the maximum OCN yield (86% at 330°C) corresponds to a yield of 75% free HNCO (*8*). Figure 5 shows the effects of the flow rate (residence time) on the proportions of N_2, NH_3, and total OCN

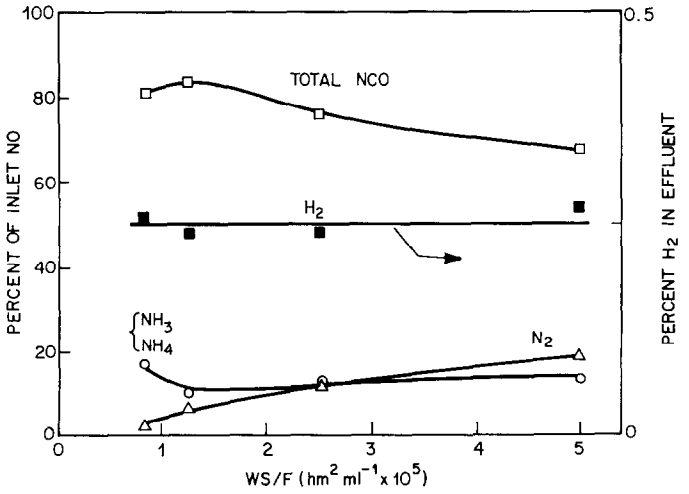

FIG. 5. Effect of the reciprocal flow rate (residence time) on the proportions of N-containing products in the effluent. Ir catalyst, prereduced as in Fig. 4a. Flow rate expressed as milliliters of gas per hour per square meter of Ir in the sample. 362°C. Feed, 0.3% NO, 0.5% H_2, 5% CO in He.

in the effluent. The data suggest that at 362°C NCO participates in consecutive reactions leading to N_2, whereas NH_3 is mostly formed in a reaction parallel to the desorption of HNCO.

Platinum–10% Rhodium

The Pt–10% Rh catalyst was available as a wire gauze with high surface area. Consequently, the volume of catalyst used at a given flow rate (in volume of gas per hour and per square meter of catalyst area in the sample) is small. This leads to space velocities in the range of GHSV = 700,000 hr^{-1}. After prereduction in flowing H_2 at 450°C for 1 hr, the yields of NH_4OCN and HNCO were as given in Fig. 6. N_2 (not shown) remained constant at about 2% of inlet N (as NO). Figure 7 shows the effect of space velocity for the conversion of NO in the presence and absence of 4% H_2O in the feed mixture. The temperature, 230°C, is in the range where NO is largely, but not completely, converted. Comparison of Fig. 7a ("dry") and Fig. 7b (4% H_2O) shows that the overall rate of NO conversion is not affected by H_2O. In Fig. 7b, formation of NH_3 is clearly a consecutive hydrolysis of NH_4OCN. In the dry system, HNCO and NH_4OCN form with similar kinetics and appear to be formed in parallel reactions (Fig. 7a).

The conversion of NO into NCO with simultaneous conversion of NO to NH_3 (to form gas-phase NH_4OCN) occurs with high yields over Pt–10% Rh (Fig. 6). However, it was shown that conversion of NO and NH_3 to NH_4OCN according to Eq. (3) is also an efficient process (Table 3). To minimize combination of NO and NH_3 to N_2, which is a well-known and fast reaction (*14, 15*) the catalyst was first heated in a mixture of 5% CO and 0.3% NO in He at 340°C for 2 hr. The results in Table 3 show that a process according to Eq. (3) can be carried out with 86% yield of NCO, based on NO. At higher concentrations of reactants (1% NO and 1% NH_3 with a stoichiometric ratio of CO (2%) corresponding to Eq. (3)), a highly selective conversion of NO to NH_4OCN was obtained (Fig. 8). Of course, the present experiments cannot exclude the possibility that part

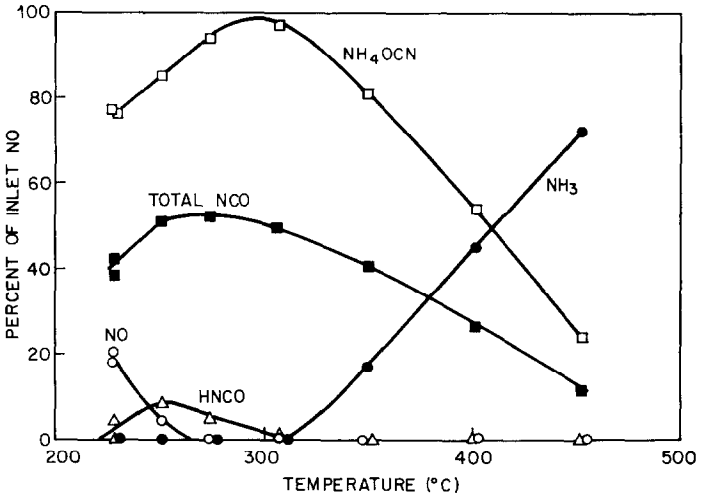

FIG. 6. Conversion of NO over Pt–10% Rh catalyst to total NCO (in HNCO and NH_4OCN), HNCO, NH_4OCN, and NH_3. All products and NO in the effluent are plotted as the percentage of N in inlet NO recovered as N-compounds. Gas mixture is 0.3% NO, 0.5% H_2, and 5% CO in He at a flow rate of 1.9×10^4 ml/hr/m^2 of catalyst in the sample.

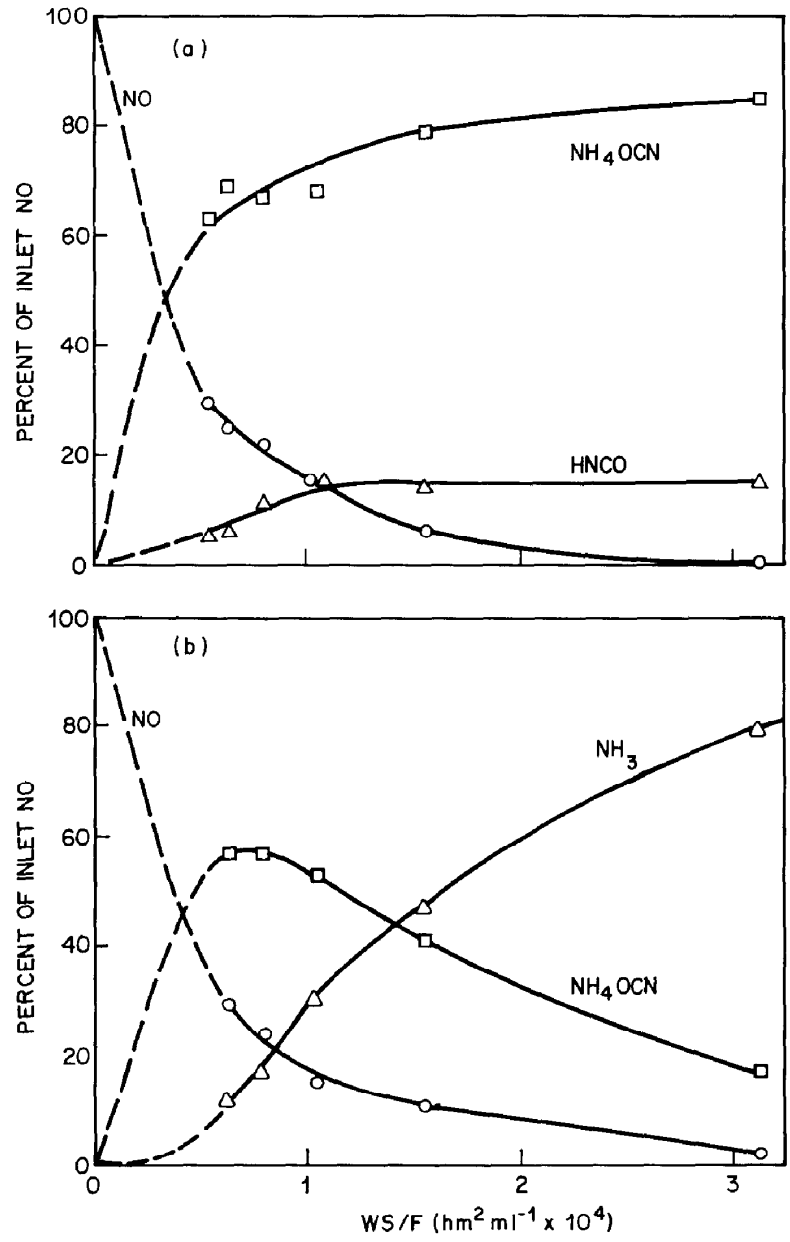

FIG. 7. Effect of reciprocal flow rate (residence time) on the proportions of N-containing compounds in the effluent. Pt–10% Rh catalyst at 230°C. Flow rates expressed in milliliters per hour per square meter of catalyst in the sample. (a) Feed mixture, 0.3% NO, 0.5% H_2, 5% CO in He. (b) Mixture as in a, with the addition of 4% H_2O.

of the NH_3 is converted to NCO, but this is not likely, since experiments aimed at converting NO and NH_3 to a larger yield than 100% NCO (based on NO) have failed under the conditions reported here, for feed ratios $1 < NH_3/NO < 3$. The results in Table 3 also show that H_2O cannot be used to replace H_2 in the reaction of Eq. (3) at temperatures where the hydrolysis of NCO is fast (compare Fig. 7b), but

TABLE 3

Conversion of NO and NH_3 into NH_4OCN over Pt–10% Rh

Temperature (°C)	Flow rate ($ml/m^2 \cdot hr$)	Inlet gas[a]		Conversion[b] of NO to	
		% H_2	% H_2O	N_2 (%)	NCO (%)
340	8.0×10^3	0.15	0	10.5	84
340	8.0×10^3	0.30	0	4.5	74.5
350	8.0×10^3	0.15	0	14	86
350	1.1×10^4	0	0.15	30	69.5
350	1.1×10^4	0	0.35	31	66
350	1.1×10^4	0	0.5	29	65
350	1.1×10^4	0	0.6	25.5	58

[a] H_2 and H_2O in addition to 0.3% NH_3, 0.3% NO, and 5% CO in He. 0.15% H_2 is stoichiometric for the reaction $2NO + 2NH_3 + H_2 + 4CO \rightarrow 2NH_4OCN + 2CO_2$, while 0.15% H_2O is stoichiometric for the reaction $2NO + 2NH_3 + H_2O + 5CO \rightarrow 2NH_4OCN + 3CO_2$. No H_2 was noticed in the effluent in any of the experiments where H_2O was added to the feed.

[b] Conversion of NO was 100%. Calculations in these columns are based on N from NO recovered as NCO or N_2. No N from NH_3 is assumed to be incorporated in NCO.

where the water–gas shift reaction does not occur.

DISCUSSION

The present work shows that 2 mol of NO can be converted to 1 mol of NH_4OCN with a yield of 97% over a commercially available Pt–10% Rh gauze at a space velocity of 700,000 (v/v) hr^{-1}. Similarly high yields were reached over Pt and Rh "sponges" (*6*, *7*). A more advantageous process, viz., converting 1 mol of NO and 1 mol of NH_3

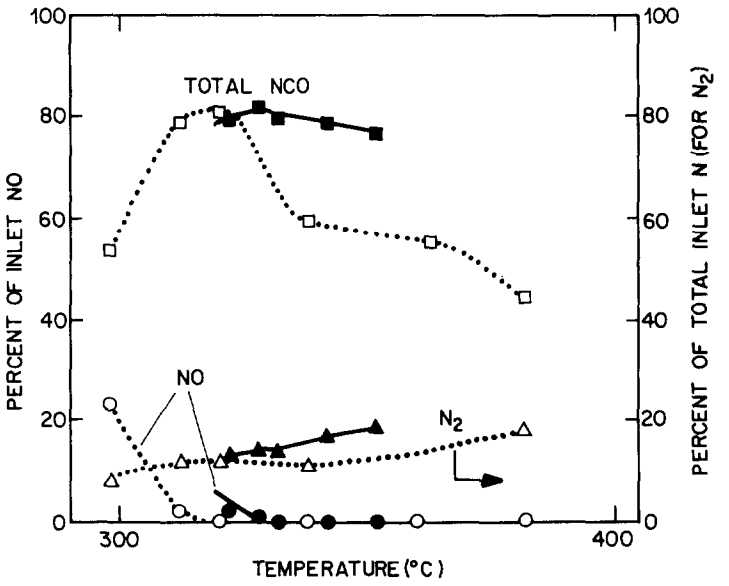

FIG. 8. Conversion of a stoichiometric mixture of 1% NO, 1% NH_3, 2% CO, and 0.5% H_2 in He into NH_4OCN over Pt–10% Rh catalyst. NCO and NO measured in the effluent are plotted as the percentage of NO in the inlet (here it is assumed that no NH_3 is converted into NCO). N_2 measured in the effluent is plotted as a percentage of the sum of NO and NH_3 entered into the reactor. Flow rates are 9.6×10^3 ml/hr/m^2 of surface area in the catalyst sample (open symbols) and 1.9×10^4 ml/hr/m^2 (filled symbols).

TABLE 4

Surface Processes in the Formation of HNCO, NH_4OCN, NH_3 and N_2 in the Reduction of NO with CO and H_2[a]

A Main reactions leading to NCO compounds	B Main reactions leading to NH_3 and N_2	C Minor reactions[b]
(1) $NO \rightarrow N(ads) + O(ads)$	(8a) $NCO(ads) + N(ads) \rightarrow N_2 + CO$	(13) $NH_2 + NO \rightarrow N_2 + H_2O$
(2) $O(ads) + H_2 \rightarrow H_2O$	(8b) $2\,NCO(ads) \rightarrow N_2 + 2CO$	(14) $CO + H_2O \rightarrow CO_2 + H_2$
(3) $O(ads) + CO \rightarrow CO_2$	(9a) $NCO(ads) + H_2O \rightarrow NH_2(ads) + CO_2$	(15) $2N \rightarrow N_2$
(4) $N(ads) + CO \rightarrow NCO(ads)$	(9b) $HNCO(ads) + H_2O \rightarrow NH_3 + CO_2$	
(5) $NCO(ads) + H \rightarrow HNCO(ads)$	(10) $NCO(ads) + H_2 \rightarrow NH_2(ads) + CO$	
(6) $HNCO(ads) \rightarrow HNCO(gas)$	(11) $NH_2(ads) + H \rightarrow NH_3$	
(7a) $HNCO(ads) + NH_3 \rightarrow NH_4OCN(gas)$	(12) $N(ads) + H_2 \rightarrow NH_2(ads)$	
(7b) $NCO^-(ads) + NH_4^+(ads) \rightarrow NH_4OCN(gas)$		

[a] "ads" refers to the adsorbed state. If no label (ads or gas) is given, the distinction is considered of no importance in the mechanism.

[b] "Minor" for the reaction conditions given in this paper and similar work. Particularly for a combination of higher temperatures and oxidized surfaces, reaction (14) is important when H_2O is added to the system.

to 1 mol of NH_4OCN with a yield of 86% is also shown to be possible over the Pt–10% Rh catalyst, at similarly high space velocities. This work also shows that HNCO can be synthesized from NO at a yield of 75% over an Ir catalyst.

The results described here for the dependence of the formation of HNCO, NH_4OCN, and other N compounds as a function of flow rate, gas composition, temperature, and catalyst serve to substantiate and refine a proposed (*8*) reaction mechanism (Table 4).

Of the reactions in Table 4, the dissociative absorption of NO at 200 to 500°C (reaction (1)) is well established by studies with infrared absorption for Ru/SiO_2 (*16*) and with low energy electron diffraction (LEED) and ultraviolet photo emission (UPS) for Ru, Rh, Pd, Pt, and Ir (*17–23*). The formation of surface (iso)-cyanate groups by the interaction of NO and CO (reaction (4)) has been established by infrared absorption for supported Pd, Rh, Ir, and Pt (*1–5*) and Ru (*16*, *24*, *25*). The hydrogenation of adsorbed NCO to form HNCO (reaction (5)) is supported by the detection of HNCO over Pd, Ir, and Pt–10% Rh (Figs. 2, 3, 6, and 7; see also Ref. *8*). The occurrence of the alternative reaction (Eq. (4)) is not supported by the data for Pt–Rh in Table 3 or for Pd in Table 2. The importance of reactions (7a) or (7b) is supported by the fact that addition of NH_3 to the feed mixture over Pt–10% Rh was found to substantially enhance the conversion of NO to NCO, rather than to NH_3 or NH_4 (compare Table 3 with data in Fig. 6). These data show that NH_3 serves to "drive HNCO off" the surface," while in its absence the formation of NH_3 is a slow process in the chain of reactions leading to formation of NH_4OCN. The participation of NH_3 in the formation of NCO was shown before to be very slow, contributing not more than 3% NH_4OCN yield over Pt at 450°C (*7*).

The reactions leading to NH_3 (reactions (9a), (9b), and (10)) include primarily hydrolysis and hydrogenation of surface NCO groups. The participation of NCO in reactions leading to NH_3 was shown by the dependence of the product distribution on the flow rate for Pt (*7*) and Pt–10% Rh (Fig. 7). Similarly, for Ir, NCO was found to participate in the formation of N_2 by reactions (8a) or (8b) (Fig. 5). Formation of NH_3 by hydrolysis of OCN (reactions (9a) and (9b)) was demonstrated at relatively low temperatures for Pt–10% Rh (compare Figs. 7a and 7b). At high

temperature the water–gas shift reaction produces H_2 from H_2O and CO and it becomes more difficult to distinguish between hydrolysis and hydrogenation of NCO intermediates (Fig. 2; see also Ref. *6*). However, the importance of the hydrogenation of NCO to NH_3 over Pt at high temperature (430°C) has been demonstrated by experiments in the absence of H_2O, in which a strong dependence of the NH_3/NH_4OCN product ratio on the flow rate was found (Fig. 2 of Ref. *7*).

The relative importance of, respectively, the desorption of NCO as HNCO or NH_4OCN (reactions (5), (6), (7a), and (7b)), the hydrolysis of NCO to NH_3 (reactions (9a) and (9b)), the hydrogenation of NCO to NH_3 (reaction (10)), and the coupling of NCO to N_2 (reactions (8a) and (8b)) depends, of course, on the catalyst as well as the temperature. It is satisfying that a clear pattern has emerged here. For any particular catalyst, it was found that prereducing the surface increased the yield of NCO products. This was so for Pt, Ir, Pd, and Pt–10% Rh. Those catalysts which are more easily reduced, such as Ir, Pt, and Rh, gave substantially higher yields of NCO products than those that are reduced only with difficulty, such as Os, Ru, and Cu–Ni. The effects of temperature are intimately connected with the oxidation state of the surface. It is a general observation for all metals used that the yield of NCO products is a maximum when NO is just completely converted. The assumption seems reasonable that as long as NO is present in the gas phase, the metal surface is partially oxidized. It is known, at least for Pt (*4*) and Ru (*24*), that the NCO intermediates are more strongly bound to partially oxidized surfaces. It is therefore expected that the surface concentration of NCO groups is a maximum at temperatures where NO is not yet completely converted. Desorptions of NCO as HNCO or NH_4OCN, i.e., reactions (6) and (7a) or (7b), are of comparable rate on such surfaces, as shown by the product distributions. NH_3 is here primarily formed by the hydrolysis reactions (9a) and (9b) and scavenged by HNCO as soon as the NH_3 is formed. This is shown by the yields near 100% of NH_4OCN over a wide range of conditions and by the effects of NH_3 added to the feed. It should be noted that our data for Pt–10% Rh show that hydrogenation of NCO to HNCO occurs faster than hydrogenation to NH_3, and this difference in rates is also in accord with the low-temperature results for Pt, Rh, Ir, and Pd.

At high temperature (i.e., well beyond the temperature where NO is completely converted), hydrogenation of NCO to NH_3 was shown to be fast over Pt (*7*) and the main reactions competing are expected to be the conversion of adsorbed NCO to NH_4OCN, its hydrogenation to NH_3 (reaction (10)), and the coupling reactions (8a) and (15). Results obtained by poisoning Pd with SO_2 show that the coupling reaction can be suppressed, leading to enhanced formation of HNCO (Fig. 3). Addition of H_2O at high temperature shows that hydrolysis of OCN is not important in that range (Fig. 2, Refs. *6–8*) if H_2 is present or easily available through the shift reaction (Table 2).

The available data on the reduction of NO over Pt and Ru in bulk or supported form (*10*, *26*) were found to be consistent with a temperature-dependent mechanism in which the formation of NH_3 was at lower temperature strongly promoted by increased concentrations of CO, whereas at higher temperature the formation of NH_3 was increased by increasing the concentration of H_2. These correlations are consistent with the mechanism summarized in Table 4. It is of interest that the effects of temperature on the concentration of NCO species measured by infrared absorption closely parallel the dependence of the formation of NH_3 over supported catalysts and the dependence of the formation

of NCO compounds on unsupported catalysts (*7*).

The reactions in Table 4 are not intended to give a detailed atomistic mechanism of the processes on the surface. The decision as to whether adsorbed or gas-phase species participate was often difficult to make and has therefore been largely avoided. Nevertheless, it is satisfying that a relatively simple picture was able to provide a consistent framework for an explanation of the effects of temperature and gas composition for all the metals investigated. In somewhat simplistic terms, the mechanism amounts to the following. In the presence of NO and CO, the metal surface becomes covered with NCO-adsorbed species which relatively slowly react to form N_2. In the presence of H_2O, slow hydrolysis leads to NH_3. H_2 is necessary to form HNCO and NH_4OCN at an appreciable rate. Too much H_2 will lead to predominant formation of NH_3, particularly at higher temperatures.

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