Synthesis of Ammonium Cyanate and Urea from NO over Pt, Os, Ru, and Cu–Ni Catalysts

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The synthesis of NH_4OCN and urea, recently reported to occur in good yields ($>90\%$) over Pt and Rh catalysts, has been studied further over Pt, Cu-Ni, Ru, and Os catalysts. The synthesis starts from NO, which is reduced to NH_4OCN with CO and H_2 diluted with He. Maximum yields of 98% at 360–400°C, 70% at 390°C, 28% at 250°C, and 10% at 250°C (based on 2 NO converted to NH_4OCN) were obtained for Pt, Cu-Ni, Os, and Ru catalysts, respectively. The effects of temperature, flow rate, reactant concentrations, and pretreatment of the catalyst were studied for Pt catalysts. The mechanism of the formation of NH_4OCN and other nitrogen products is considered. Adsorbed NCO entities appear to play a central role as intermediates.

INTRODUCTION

Recently, it was reported that the isomers of N_2H_4CO, viz., ammonium cyanate (NH_4OCN) and urea [$(NH_2)_2CO$], were formed when NO in concentrations of 0.3 to 2% in inert gas at atmospheric pressure was reduced with CO and H_2 over Pt, Rh, and Ru catalysts [1]. That report also contained a review of the relevant earlier literature. Condensation of N_2H_4CO at low temperature ($<60°C$) produced NH_4OCN, whereas, at higher temperatures (~ 80–$120°C$), urea was collected, apparently because of rapid conversion of the primary product NH_4OCN into urea after condensation in the collector. The study of the primary process [Eq. (1)] on various catalyst surfaces,

$$2NO + 2H_2 + 3CO \rightarrow$$
$$NH_4OCN + 2CO_2, \quad (1)$$
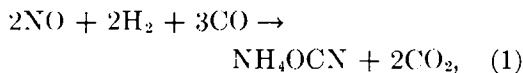
under a variety of conditions is here pursued for two reasons. First, it may yield information on the surface chemistry of the inter-action of NO, CO, and H_2 on metals and, in particular, about the role of NCO intermediates adsorbed on the surface [see references to infrared absorption studies of NCO in Ref. (1)]. Second, the process of converting NO with CO and H_2 or H_2O to N_2H_4CO at atmospheric pressure and at 300–400°C might be an economical alternative route to the two isomers, NH_4OCN and $(NH_2)_2CO$. It may be noted that economical alternatives to the conventional liquid-phase high-pressure carbamate urea process are not now available [2]. Although the cost of NO as a raw material is relatively high, this might in fact be overcome by the simplicity and high yield of the new process and by its ability to employ the dilute streams of NO produced by radiative processes [3], by high-temperature combustion as in the "Wisconsin process" [4], or as tail gas from the manufacture of nitric acid. Application of the new process in conjunction with HNO_3 manufacture might allow the latter to be

TABLE 1

Characterization of Catalysts Used

Code	Composition	Preparation	Surface area[a] (m²/g)	Ref.[b]
Pt sponge	Pt, 99.99%	Engelhard sponge	0.12	(1, 11, 12)
Ru	Ru 99.999%	Engelhard powder	1.28	(7)
Cu–Ni	Cu:Ni = 0.64:1 (at/at); Cu + Ni = 97 wt%[c]	Fillings of commercial monel alloy	0.12	(10)
Os I	Os (99.99%)	Powder (Engelhard) in reactor reduced in H₂ at 100°C for 16 hr, then at 200°C for 1.4 h, and at 350°C for 45 min		
Os II	Os (99.99%)	Os I, further reduced in the reactor at 450°C for 16 h in 90% H₂ in He		

[a] Determined by N_2 chemisorption in a Perkin–Elmer sorption meter.
[b] References to earlier work in this laboratory on the same catalyst.
[c] Analysis by Fairfield Testing Labs, Fairfield, N.J.

operated with much higher NO levels in the tail gas.

In the present report, the process as catalyzed by Pt, Os, Ru, and Cu–Ni is described, with emphasis on the most effective of these catalysts, Pt. It is shown that the yields of NH_4OCN correspond with the published concentrations of NCO (isocyanate) surface species produced by interaction of NO and CO on supported Pt and Ru catalysts and measured by infrared absorption by Solymosi et al. (5, 6). The mechanism of the formation of N_2H_4CO from NO, CO, and H_2 is considered.

EXPERIMENTAL METHODS

Since all experimental methods used have been described elsewhere, only a brief description will be given here. All experiments were carried out with a quartz fixed-bed reactor. The catalysts (1–5 g, Table 1) were supported on a fritted quartz disk. The reactant gases were obtained premixed in He from Scientific Gas Products, Freehold, N. J., and were blended in line with the aid of Brooks Co. flow controllers to obtain a feed-gas mixture of 0.3–2.0% NO,

0–2.0% H_2, 0.4–5.0% CO, and 0–2.2% O_2 in He. Water was added as appropriate. The effluent from the reactor was split for on-line gas chromatographic and colorimetric analysis. Gas chromatographic analysis was used for NO, N_2, CO, and H_2 (7). The conversion of NO to NH_4OCN was measured continuously by quantitative absorption of NH_4OCN from the effluent, conversion into urea, and colorimetric determination of urea (8) as its yellow complex with diacetyl monoxime (9). Condensed crystalline products trapped from the effluent were analyzed by ir absorption and identified as NH_4OCN and $(NH_2)_2CO$ (1). No quantitative analysis was done for NH_3, N_2O, and HCN. Earlier data on the same catalysts showed that the formation of HCN accounts for less than 1% of converted NO in the temperature range employed in the present work (10). It was also shown previously that quantitative analysis for NH_3 accounts for the balance of the N derived from NO at temperatures above 400°C (10, 11). Deficits in the N balance below about 350°C are assumed to be due to formation of N_2O.
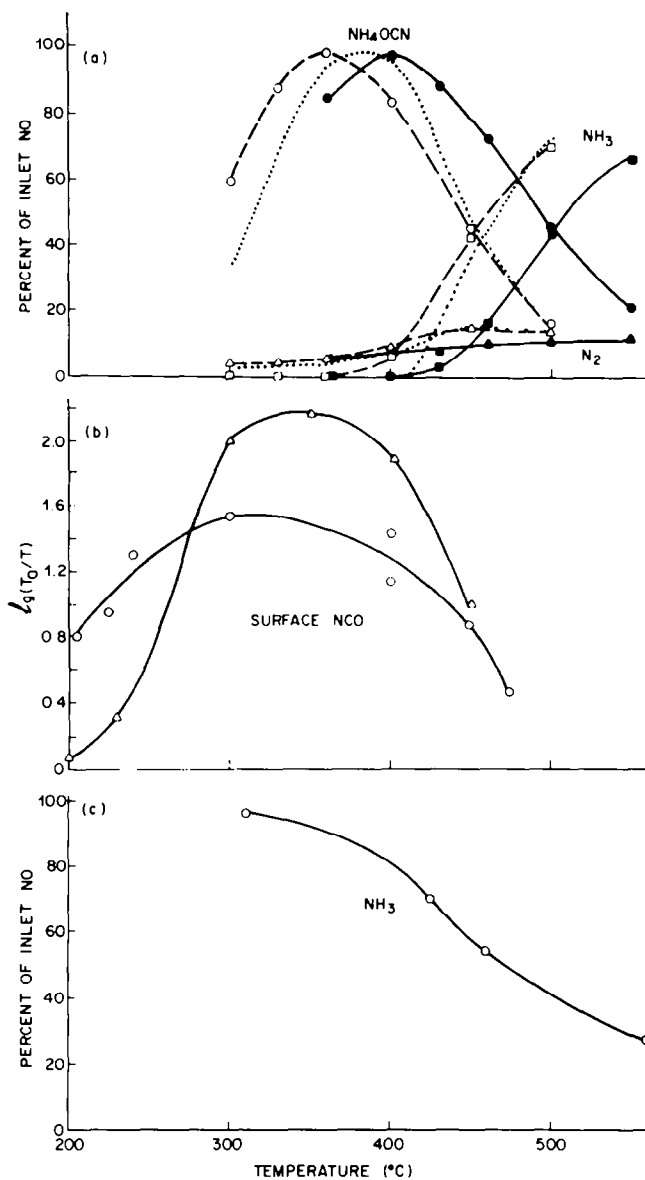
FIG. 1. Conversion of NO over Pt sponge. (a) Percentage of N in inlet NO recovered as NH_4OCN, NH_3, and N_2 is plotted. Prereduced catalyst. Flow rates, normalized per square meter of Pt in the sample, are 1.15×10^4 (- - - and symbols), 2.3×10^4 [...., from ref. (1)], and 4.0×10^4 (-·— and filled symbols) ml/h/m². Standard concentrations of NO (0.3%), H_2 (0.5%), and CO (5%). (b) Isocyanate groups on the surface of 5% Pt/Al_2O_3 measured by ir absorption at 2267 cm⁻¹: (○) reduced sample; (△) oxidized sample, after Solymosi et al. (5); (c) NH_3 formed in the reduction of 0.1% NO with 1.4% H_2 and 1.5% CO over a Pt/Al_2O_3 catalyst, after Shelef and Gandhi (16).

RESULTS

Platinum

The formation of NH_4OCN, NH_3, and N_2 from a "standard mixture" (0.3% NO,

0.5% H_2, and 5% CO in He) over a Pt sponge catalyst is given in Fig. 1 as a function of the temperature of the catalyst. Three values of the flow rate were used, viz., 1.15×10^4, 2.3×10^4, and 4.0×10^4
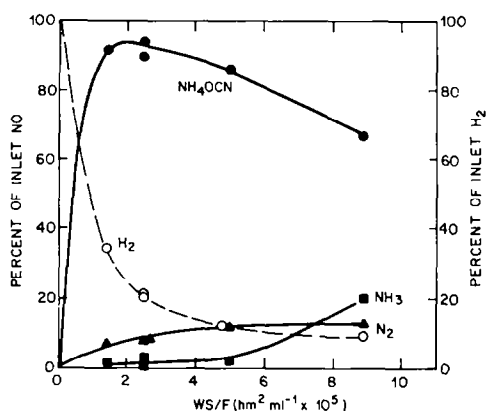
ml/h/m² of Pt in the sample, respectively.
This corresponds to GHSV values of 6800
to 23,500 h⁻¹. The data for 2.3×10^4 ml/
h/m² are from Ref. (1). Prior to use, the
catalysts were reduced in 2% H_2 in He at
475–500°C for 11 h or longer. Without
prereduction, the results are similar to
those in Fig. 1, except that the yields of
N_2 are somewhat higher and the yields of
NH_4OCN are correspondingly lower. The
effect of increasing flow rate is primarily
to shift the yield curves, including the op-
timum yield of NH_4OCN, to higher tem-
perature. This optimum, which is close to
100%, is in all cases reached at the tem-
perature at which NO is just completely

converted (NO is not shown for clarity).
Figure 2 shows the effect of reciprocal flow
rate on the conversion of NO into N_2, NH_3,
and NH_4OCN over the same catalyst (Pt
sponge) at 430°C. NH_4OCN appears to be
a primary product, followed by formation
of NH_3.

The composition of the feed gas has been
varied to study the effects on the yield of
NH_4OCN. At constant levels of NO and H_2
(0.3% each), the concentration of CO has
been varied from 0.4–5.0%. Figure 3 shows
the results of two series of experiments: one
with a freshly reduced Pt sponge and the
other with the same Pt sponge after it had
been stored under He for 4 days without
regeneration and apparently had lost some
of its selectivity. The temperature for both
series was 404°C, and the flow rate was
4.0×10^4 ml/h/m². The variations of the
yield with the concentration of CO are
similar in both series; a substantial drop in
selectivity occurs only below 2% CO. For
the reaction of Eq. (1), this corresponds to
a fourfold excess of CO. For the less selec-
tive, used catalyst, the effect of increasing
the concentrations of NO and H_2 (at
$NO/H_2 = 1.0$) at a constant CO concen-
tration (5%) is given in Fig. 4. A significant
decline in selectivity occurs here when the
amount of CO is less than 2.5 times the
stoichiometric amount.
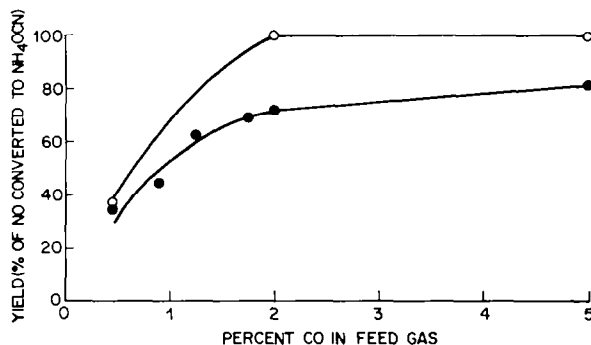
Industrial streams containing NO often
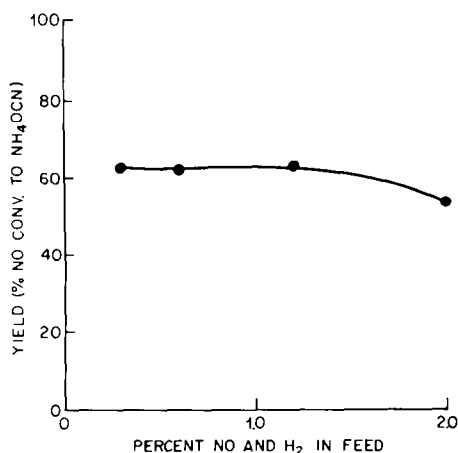
contain O$_2$ and H$_2$O. Figure 5 shows the effect of adding O$_2$ to the standard gas mixture, maintaining NO, H$_2$, and CO at 0.3, 0.5, and 5%, respectively. The catalyst is the Pt sponge and the flow rate is 2.3 × 10^4 ml h m^2. Series of experiments at 409 and 500°C are shown. At 409°C, a deleterious effect of O$_2$ on the yield of NH$_4$OCN is noted only beyond 2.2% O$_2$, i.e., when the amount of O$_2$ is close to the stoichiometric amount necessary for Eq. (1) plus oxidation of CO. At 500°C, small amounts of O$_2$ in the feed gas enhance the yield of NH$_4$OCN at the expense of NH$_3$.
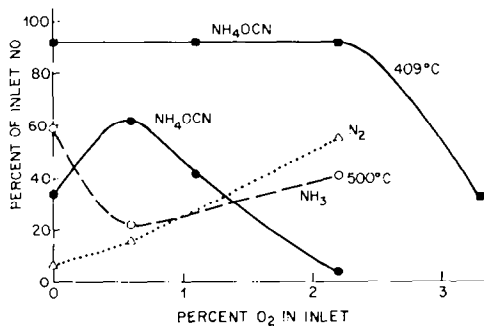

FIG. 5. Effect of O$_2$ on the conversion of NO over Pt sponge at 409 and 500°C. Prereduced catalyst. Flow rate: 2.3×10^4 ml/h/m^2. Standard concentrations of NO (0.3%), H$_2$ (0.5%), and CO (5.0%).

TABLE 2

Formation of NH$_4$OCN from NH$_3$ over Pt Sponge[a]

| Experiment No.	Gas composition (% in He)				T (°C)	Conversion of NH$_3$ to NH$_4$OCN (%)
	NH$_3$	CO	CO$_2$	O$_2$		
1	1.33	0.67			450	1.6
2	1.33	0.67		0.05	450	2.0
3	0.3	1.7			450	3.2
4	1.33		0.67		450	0
5	0.3		1.7	0.15	380	0.3
6	0.3		1.7	0.3	380	0.7

[a] Flow rate: 1.15 × 10^4 ml/h/m^2.

Beyond the addition of 1.2% O$_2$, the yield of NH$_4$OCN is diminished with respect to the O$_2$-free reaction mixture. The effect of water on the yield of NH$_4$OCN has been reported previously (1). Water could be used instead of H$_2$ to supply H for N$_2$H$_4$CO in the temperature range near 400°C (1). At lower temperatures, near those where NO is first completely converted, hydrolysis of cyanate to NH$_3$ was observed to occur at relatively high rates (13).

Since there have been reports (14, 15) that NH$_3$ may react with CO or CO$_2$ according to

$$CO + 2NH_3 \rightarrow N_2H_4CO + H_2 \qquad (2)$$

and

$$CO_2 + 2NH_3 \rightarrow N_2H_4CO + H_2O, \qquad (3)$$
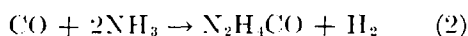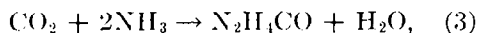
we have attempted these reactions over the fresh, prereduced Pt sponge catalyst to ascertain whether NH$_3$ formed in the reduction of NO could be an intermediate in the formation of the cyanate group. With gas mixtures containing NH$_3$ (0.3–1.3%), CO (0.6–1.7%), and O$_2$ (0–0.05%) in He or NH$_3$ (0.3–1.3%), CO$_2$ (0.6–1.7%), and O$_2$ (0.15–0.3%) in He, at a flow rate of 1.15 × 10^4 ml h m^2 and in the temperature range of 250–550°C, a maximum yield of NH$_4$OCN (calculated on NH$_3$ inlet) of 3% was obtained. The "best" yields were obtained with a mixture of 0.3% NH$_3$ and
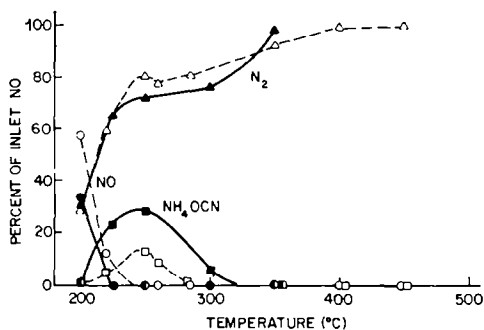
FIG. 6. Conversion of NO over Os catalyst. Percentage of N in inlet NO recovered as NO, N₂, and NH₄OCN is plotted. Flow rate: 4.6×10³ ml/h/m² of Os in the sample. Standard concentrations of NO (0.3%), H₂ (0.5%), and CO (5.0%) in He. Heavy lines and filled symbols: Os I catalyst. Light lines and open symbols: Os II catalyst.

1.7% CO. Small additions of O₂ increased the yield (Table 2).

Osmium and Ruthenium

A very gradual prereduction of the Os metal powder was used to prevent the evolution of highly volatile OsO₄ (Table 1). The results in the reduction of NO were found to be susceptible to the oxidation state of the catalyst to a stronger degree than was the case for Pt. Figure 6 shows that N₂ is the predominant product of the reduction. The standard mixture of NO, H₂, and CO in He was used at a rate of flow of 4.6 × 10³ ml/h/m². A moderate prereduction of the catalyst gave a higher yield of NH₄OCN (28% at 250°C) than a more thorough prereduction procedure (which yielded 13% at 250°C).

A study of the reduction of NO with CO and H₂ over Ru was published before (7). The yield of NH₃ showed two peaks, centered at approximately 250 and 380°C. The same catalyst was used in the present experiments. Figure 7a shows the yield of NH₄OCN, with a maximum near 240°C, observed with the standard mixture of gases used at a flow rate of 1.2 × 10⁴ ml/h/m². The peak value of 10.5% decreased to 6% when the flow rate was cut in half.
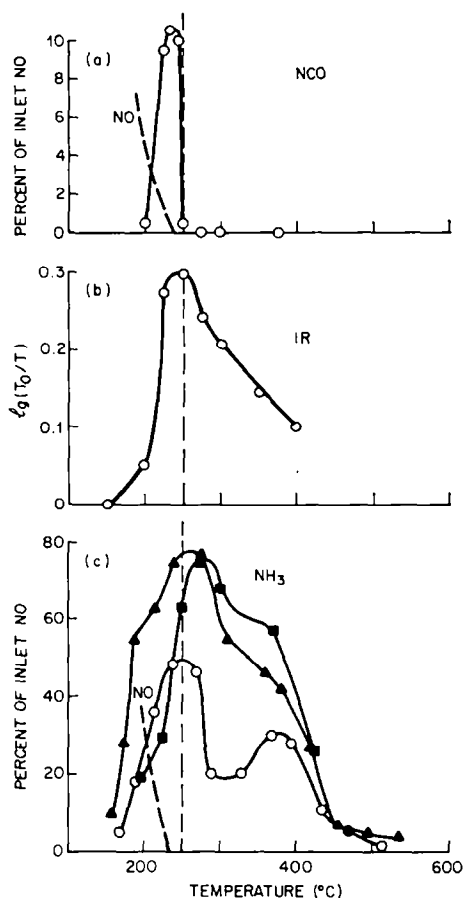

FIG. 7. Ru in the interaction of NO, CO, and H₂. (a) Present work. Percentage of N in inlet NO recovered as NH₄OCN and NO versus catalyst temperature. Prereduced unsupported catalyst. Standard gas mixture of NO (0.3%), H₂ (0.5%), and CO (5%) in He at a flow rate of 1.2×10⁴ ml/h/m², corresponding to a GHSV of 90,000 h⁻¹. (b) Concentration of NCO surface species on a reduced 5% Ru/Al₂O₃ catalyst after 30 min of contact with 100 Torr of a mixture of 5% NO, 10% CO, and 85% N₂ at the temperature indicated. Measured by ir absorption (2265 cm⁻¹) at room temperature by Solymosi and Rasko (6). (c) Yield of NH₃ in the reduction of NO with H₂ and CO (○) Data on unsupported Ru sponge, with mixture W of NO (0.13%), H₂ (0.4%), CO (1.3%), H₂O (3%), and CO₂ (3%) in He at GHSV = 33,000 h⁻¹, after Voorhoeve and Trimble (7); (▲) data on a reduced 0.8% Ru/Al₂O₃ catalyst with the same mixture W at GHSV = 18,000 h⁻¹ (7); (■) data on a 0.5% Ru/Al₂O₃ catalyst with a mixture of NO (0.1%), H₂ (1.4%), and CO (1.5%) in N₂ at GHSV = 20,000 h⁻¹, after Shelef and Gandhi (16).

Monel (Cu Ni)

The catalyst was prereduced in flowing pure H_2 at 450°C. Figure 8 shows the conversion of NO into N_2 and NH_4OCN in dependence of the temperature of the catalyst. The standard gas mixture was used at a flow rate of 1.6×10^4 ml h/m². The maximum yield of NH_4OCN was 70%. In an interval of 10°C this decreases to 0%. This behavior was reproducible, and the steep section of the yield–temperature curve could be traversed in both reactions with no hysteresis. There was no corresponding feature in the yield of N_2.

DISCUSSION

In the data collected for Pt, it is striking that a very high yield of NH_4OCN was obtained over a wide range of operating conditions (Figs. 1–3). It is particularly evident that NH_4OCN and N_2 are the only products over an appreciable range of low-temperature ($\lesssim 400°C$) conditions. No isocyanic acid (HNCO) was detected. This strongly suggests that NCO intermediates on the surface can only desorb as NH_4OCN, i.e., that a step like

$$NCO \cdot + NH_4^+ \rightarrow NH_4OCN \quad (4a)$$

or

$$HNCO(ads) + NH_3 \rightarrow NH_4OCN, \quad (4b)$$
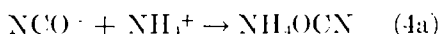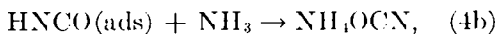
due to the lack of NH_3, is the rate-determining step in the conversion of NO to cyanate in the gas phase. It has indeed been found that the addition of NH_3 to the feed strongly enhances the conversion of NO to cyanate over a Pt–10% Rh catalyst (13). At temperatures of 400°C and below, surface NCO groups are rather stable on Pt in the presence of NO and CO. The amount of NCO found by ir absorption after contacting (at temperature T) a Pt/Al_2O_3 catalyst with NO/CO mixtures with an excess of CO shows a dependence on T which is rather strikingly similar to the temperature profile of NH_4OCN forma-
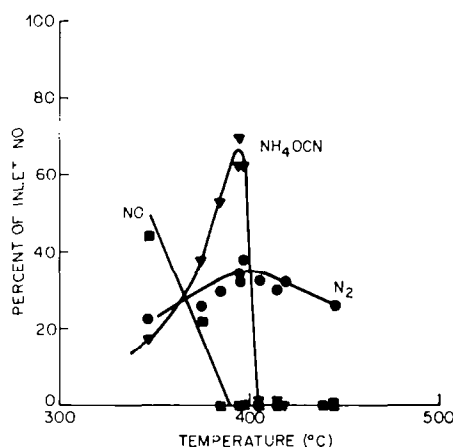

FIG. 8. Conversion of NO over a Cu-Ni (monel) catalyst. Percentage of N in inlet NO recovered as NO, N_2, and NH_4OCN. Prereduced unsupported catalyst. Standard gas mixture at a flow rate of 1.6×10^4 ml/hr/m².

tion in Fig. 1, except that the NCO peak measured by ir extends to lower temperature (5). Removal of NCO from the surface is, at low temperature ($\lesssim 400°C$), proposed to be limited by the prerequisite hydrolysis of NCO to form NH_3, a reaction first proposed by Unland (17, 18):

$$NCO^- + 2 H_2O \rightarrow NH_3 + OH^- + CO_2.$$

$$(5)$$
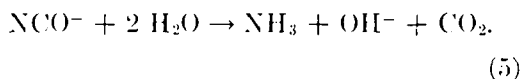
On oxidic surfaces such as provided by the oxide support [to which NCO groups may migrate (19)], Eq. (5) may reasonably be expected to dominate over Eq. (4a) or (4b), in agreement with the experience (1) that NH_3 rather than NH_4OCN is the main product for the reduction of NO with CO and H_2 (or H_2O) over Pt/Al_2O_3 catalysts. At low temperature, NCO is relatively unreactive to H_2, on both Pt/Al_2O_3 and Pd/Al_2O_3 (18, 20) suggesting again that hydrolysis, rather than hydrogenation, is the preferred route to NH_3 at $T \lesssim 400°C$. The hydrolysis is slow on unsupported Pt, however, and high yields of NH_4OCN were obtained even in the presence of 5% H_2O at 400°C (1). However, at higher temperatures hydrogenation of the NCO or

NH₄OCN species is possible, as shown by the increase of NH_3 formation at the expense of NH_4OCN when the concentration of H_2 is increased (1, 13). A consecutive reaction,

$$NH_4OCN + H_2 \rightarrow 2\ NH_3 + CO,\quad (6)$$
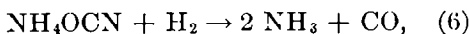
is in agreement with the data for 430°C in Fig. 2 which show that NH_4OCN is a primary product, whereas free NH_3 is only formed at much longer residence times. Finally, the data in Fig. 5 show that preferential removal of H_2 with O_2 increases the yield of NH_4OCN and decreases the yield of NH_3 at 500°C, in agreement with the reaction scheme of Eqs. (4)–(6). Comparison of Fig. 1c with Figs. 1a and b suggests that the formation of NH_3 on Pt/Al_2O_3 may very well be accounted for by hydrolysis and hydrogenation of cyanate intermediates. Naturally, such a cross correlation of data from different sources cannot be definitive.

The mechanisms of the formation of NH_4OCN and NH_3 over Rh (1), Cu-Ni, Ru, and Os are expected to be similar, but, of course, the relative yields of the various products will be different due to different oxidation states of the surfaces and different relative rates of the various processes. Isocyanate or cyanate surface species have been reported in studies of the interaction of CO and NO with Ru/Al_2O_3 (6, 17) and CuO/SiO_2 (21), as well as with Rh/Al_2O_3 (17, 22).

Figure 7 shows that (for Ru) the three phenomena (NH_4OCN formation, detection of NCO at the surface by ir, and production of NH_3 by reduction of NO) appear to be related in a similar way as in the case of Pt. It should be noted that the formation of NH_3 over Ru catalysts was reported to be promoted by CO in the range of the low-temperature peaks in Fig. 7c (7, 16, 23), whereas the high-temperature NH_3 peak was promoted by H_2 (7). The correlation extends to the relative stability of NCO and the yield of NH_4OCN:

Stability (6) and yield are much lower for Ru than for Pt catalysts. Finally, it is noted that the rates of formation of NH_4OCN and of NH_3 are comparable in the temperature range in which the cyanate is proposed to be an intermediate for the formation of NH_3 (200–300°C). There is no evidence for cyanate as an intermediate or product over Ru at higher temperatures.

CONCLUSIONS

Reduction of NO with CO and H_2 over unsupported Pt catalysts is an efficient, high-yield process for the formation of ammonium cyanate and urea. Yields of 95% have been obtained at temperatures of 400°C and below, with complete conversion of NO. There is mounting evidence for the important role of (iso)cyanate surface species as crucial intermediates in the formation of NH_4OCN and NH_3. The reactions of the NCO intermediate are likely to include hydrolysis to NH_3, desorption as NH_4OCN after reaction with NH_3, and hydrogenation to NH_3. At low temperature ($<400°C$), desorption and hydrolysis dominate, whereas, at higher temperature ($>400°C$), hydrogenation becomes important.

REFERENCES

1. Voorhoeve, R. J. H., Trimble, L. E., and Freed, D. J., Science, in press.
2. Standen, A. (Ed.), "Kirk Othmer's Encyclopedia of Chemical Technology", Vol. 21, p. 37. Interscience, New York, 1965.
3. Harteck, P., and Dondes, S., Science 146, 30 (1948).
4. Gilbert, N., and Daniels, F., Ind. Eng. Chem. 40, 1719 (1948).
5. Solymosi, F., Sarkany, J., and Schauer, A., J. Catal. 46, 297 (1977).
6. Solymosi, F., and Rasko, J., J. Catal. 49, 240 (1977).
7. Voorhoeve, R. J. H., and Trimble, L. E., J. Catal. 38, 80 (1975).
8. Trimble, L. E., and Voorhoeve, R. J. H., Analyst, in press.
9. Fearon, W. R., J. Biochem. 33, 902 (1939).
10. Voorhoeve, R. J. H., Patel, C. K. N., Trimble, L. E., and Kerl, R. J., J. Catal. 45, 297 (1976).
11. Voorhoeve, R. J. H., Patel, C. K. N., Trimble, L. E., and Kerl, R. J., J. Catal., in press.

12. Voorhoeve, R. J. H., Patel, C. K. N., Trimble, L. E., and Kerl, R. J., *Science*, 190, 149 (1975).
13. Voorhoeve, R. J. H., and Trimble, L. E., *J. Catal.*, in press.
14. Jackson, H., and Northall-Laurie, D., *J. Chem. Soc.* 87, 433 (1905).
15. Kucheryavyi, V. I., Gorlovski, D. M., Altshuler, L. N., Zinovev, G. N., Karlik, A. B., and Klopina, N. A., U. S. S. R. Author's Certificate 371210, 1973.
16. Shelef, M., and Gandhi, H. S., *Ind. Eng. Chem. Prod. Res. Develop.* 11, 393 (1972).

17. Unland, M. L., *J. Catal.* 31, 459 (1973).
18. Unland, M. L., *J. Phys. Chem.* 77, 1952 (1973).
19. Dalla Betta, R. A., and Shelef, M., *J. Mol. Catal.* 1, 431 (1976).
20. Solymosi, F., and Sarkany, J., *React. Kinet. Catal. Lett.* 3, 297 (1975).
21. London, J. W., and Bell, A. T., *J. Catal.* 31, 96 (1973).
22. Arai, H., and Tominaga, H., *J. Catal.* 43, 131 (1976).
23. Taylor, K. C., and Klimisch, R. L., *J. Catal.* 30, 478 (1973).