Reports

Synthesis of Ammonium Cyanate and Urea by Reduction of Nitric Oxide on Platinum, Rhodium, and Ruthenium Catalysts

Abstract. *Nearly quantitative conversion of nitric oxide (NO) into N_2H_4CO has been obtained in the reduction of NO with carbon monoxide and hydrogen over platinum and rhodium catalysts. Depending on the temperature of collection, N_2H_4CO is isolated as ammonium cyanate or its isomer, urea. The process is an effective way of recovering fixed nitrogen from dilute industrial streams containing NO. Ammonium cyanate may play a role in the reduction of NO in automotive exhaust control.*

Reduction of NO with CO and H_2 is an important process in the control of the emissions of nitrogen oxides from internal combustion engines and in the stack gases of industrial processes. The objective in control systems is to reduce NO to N_2, but considerable conversion to undesirable products such as NH_3 (*1*) and HCN (*2, 3*) is often obtained. On the other hand, in the production of "fixed" nitrogen as NO, the recovery of NO from dilute gas mixtures is a difficult and inefficient process that places a heavy fiscal burden on fixation processes such as the direct oxidation of nitrogen. In this report we describe the conversion of NO and CO into ammonium cyanate (NH_4OCN) and explore its implications for the catalytic control of automotive exhaust emissions and for the recovery of fixed nitrogen from dilute streams containing NO.

Formation of isocyanate (*4*) surface species in the reduction of NO with CO was detected by infrared (IR) absorption on Ru, Rh, Pd, Pt, and Ir dispersed on Al_2O_3 by Unland (*5*) and on Cu_2O dispersed on SiO_2 by London and Bell (*6*). Later IR absorption studies on Ru/SiO_2 (*7*) and Rh/Al_2O_3 (*8*) also showed formation of isocyanate surface species. Solymosi and co-workers (*9–11*) compared the formation of isocyanate species on the surfaces of Pt/Al_2O_3, Pd/Al_2O_3, and Ru/Al_2O_3 as a function of temperature and concluded that the NCO groups were much more stable on Pd and Pt than on Ru. Thus, the formation of NCO groups by the interaction of CO and NO on the surfaces of supported metallic catalysts seems well established. However, their role in the mechanism of the formation of NH_3 by reduction of NO with CO and H_2 and Unland's proposal that the hydrolysis of NCO intermediates may be a major pathway to NH_3 (*5*) have been vigorously disputed (*12*).

Formation of gaseous products with OCN or NCO groups (cyanates or isocyanates) was not detected in the IR studies cited and to our knowledge has not been reported for the reduction of NO (*13*). We have found that nearly quantitative conversion of NO to N_2H_4CO (*4*) may be achieved. Depending on the collection temperature, either NH_4OCN or its isomer, urea $[(NH_2)_2CO]$, is collected as a solid product.

The bench-scale reactor and the analysis of the compounds N_2, N_2O, NO, CO, CO_2, and H_2 by gas chromatography have been described in detail (*14*). Briefly, a mixture of NO (0.3 to 2.0 percent), H_2 (0 to 2.0 percent), CO (0.4 to 5.0 percent), O_2 (0 to 3.3 percent), and H_2O (0 to 5 percent) in He is passed over a catalyst supported on a fritted quartz disk in a tubular quartz reactor. The effluent from the reactor is split. One part is dried and analyzed over Porapak Q and molecular sieve type 13X columns in a gas chromatograph with a thermal conductivity detector. The other part of the effluent is scrubbed in an absorber designed to prevent condensation of solid NH_4OCN. The NH_4OCN in solution is converted quantitatively into urea (*15*) and the urea in solution is determined colorimetrically as the yellow complex with diacetylmonoxime (*16*). The method as developed (*17*) yields a continuous analysis of NH_4OCN in the gas phase with a sensitivity of 0.4 part per million (ppm) and an accuracy of 2 percent at concentrations of 20 ppm to 1 percent in the gas phase. The products of the reaction have also been collected in a condenser and analyzed by IR absorption.

The catalysts employed were two lots of Pt sponge with surface areas of 0.12 and 0.05 m^2/g, respectively; one lot of Rh sponge with a surface area of 1.69 m^2/g; and one lot of Ru with a surface area of 0.4 m^2/g (*18*). Supported Pt catalysts included a PTX-3 containing Pt dispersed on an Al_2O_3 wash coat on a cordierite support and a 0.5 percent Pt on Al_2O_3 catalyst.

Results. The yield of NH_4OCN obtained from a mixture of 0.3 percent NO, 0.5 percent H_2, and 5 percent CO in He (the "standard gas mixture") reacted over one of the Pt catalysts was studied as a function of the pretreatment of the catalyst, the flow rate, and the temperature. The pretreatment of the Pt sponge had a discernible effect on the yield, but for each lot of catalyst an optimum pretreatment involving reduction in H_2 was established by trial and error. Figure 1 shows the composition of the effluent from the Pt catalyst as a function of catalyst temperature. The NH_4OCN, NO, and N_2 in the effluent are expressed as mole percentages of the NO in the inlet gas; for example, 100 percent NH_4OCN means that all NO is converted into NH_4OCN. The data in Fig. 1 show that NO is converted into NH_4OCN with better than 85 percent selectivity between 300° and 400°C, the remainder of the product being N_2. Above about 420°C, the selectivity is diminished by competitive formation of NH_3. The pattern of Fig. 1 is not materially affected by flow rate. Increasing the flow rate to 7×10^4 ml/hour per square meter of Pt in the sample displaced the pattern to higher temperatures, but very similar yields were attained at the optimum. The best yields obtained were around 95 percent.

Conversion of the standard mixture of NO, CO, and H_2 over Rh shows a very similar dependence of the yield of NH_4OCN on temperature (Fig. 2), with a maximum conversion of NO to NH_4OCN of 92 percent. Unlike the case of Pt, Rh promotes the formation of nitrogenous products other than NH_4OCN and N_2 at low temperatures. Where the nitrogen balance showed a deficit, it was assumed on the basis of earlier analyses (*14*) that the rest of the NO was converted to NH_3 at high temperatures and to N_2O at low temperatures, but no independent quantitative analysis of these compounds was made.

When passed over the Ru catalyst, the standard mixture of NO, CO, and H_2 in He yielded only minor amounts of NH_4OCN. The maximum yield obtained, at 240°C, was 10 percent, calculated on the basis of converted NO.

To assess the importance of the conversion of NO to NH_4OCN within the context of automotive exhaust con-

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version and of recovery of NO from dilute manufacturing streams, we determined the yield of NH_4OCN as a function of the composition of the gas, varying the concentrations of NO, CO, O_2, H_2, and H_2O within the limits specified above (*19*). Briefly, addition of up to 2.2 percent O_2 to the standard mixture at 409°C did not affect the yield of NH_4OCN over Pt at all. At 404°C, also with a Pt catalyst, it was found that variations of the concentration of CO between 2 and 5 percent did not affect the yield of NH_4OCN, but that a decrease of CO below 2 percent (in the presence of 0.3 percent NO and 0.5 percent H_2) decreased the yield of NH_4OCN. The concentrations of NO and H_2 were varied at 420°C over Pt, keeping the concentration of CO at 5 percent. The NO/H_2 ratio was kept at 1.0. The yield of NH_4OCN was nearly insensitive to the NO and H_2 concentrations up to NO = H_2 = 2 percent. Finally, the effect of H_2O on the conversion reaction was studied. The results in Table 1 show that in the range of optimum temperatures H_2O does not inhibit the formation of NH_4OCN over Pt catalysts. Evidently, the hydrolysis reactions

$$OCN^-(ads) + 2H_2O \rightarrow NH_3 + OH^-(ads) + CO_2$$

and

$$NH_4OCN + H_2O \rightarrow 2NH_3 + CO_2$$

[where (ads) means adsorbed] are slow over the metallic catalysts in this temperature range near 400°C. The third experiment in Table 1 shows that H_2O can actually take the place of H_2 as a source of hydrogen for the formation of NH_4OCN. It is likely that H_2 is formed from H_2O and CO through the water-gas shift reaction. The effect of SO_2 was not measured for these catalysts. However, it is of interest to note that over a Pd catalyst, introduction of SO_2 did not diminish the yield of NH_4OCN (expressed as the percentage of NO converted), even though the overall activity of the catalyst was diminished (*19*).

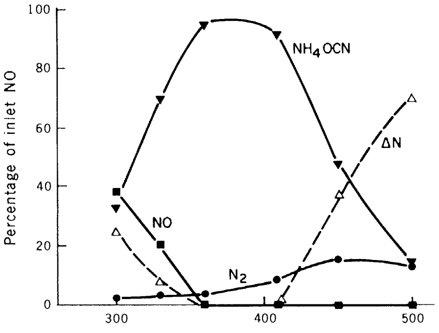

Fig. 1. Formation of NH_4OCN and N_2 in the reduction of NO with H_2 and CO over a Pt sponge catalyst (surface area, 0.12 m^2/g). The flow rate was 2.3×10^4 ml/hour per square meter of Pt surface in the sample. The gas mixture was 0.3 percent NO, 0.5 percent H_2, and 5 percent CO in He. Platinum was reduced before use for 16 hours at 475°C in 2 percent H_2 in He. The dashed line shows the deficit in the nitrogen balance, primarily due to formation of N_2O below 350°C and of NH_3 above 400°C.

Table 1. Formation of NH_4OCN over a Pt catalyst at 420°C in a gas mixture of NO, CO, H_2, and H_2O in He at a flow rate of 4×10^4 ml/hour per square meter of Pt surface in the catalyst sample.

Inlet gas composition* (%)				Yield of NH_4OCN† (%)
NO	CO	H_2	H_2O	
0.6	5.0	0.6	0.0	63.0
0.6	5.0	0.6	4.3	77.5
0.6	5.0	0.0	4.3	69.0
0.3	2.0	0.5	0.0	62.0
2.0	5.0	2.0	4.5	61.0

*The balance is He. †Calculated as moles of NH_4OCN produced per 200 moles of NO converted. In all these experiments, NO was completely converted.

The solid products obtained by conversion of the standard mixture into N_2H_4CO were collected at the optimum catalyst temperature. They were diluted with KBr (3:100), pressed into pellets, and analyzed by IR absorption spectroscopy. The spectrum of the condensate collected at room temperature showed that it was virtually pure (~ 98 percent) NH_4OCN (NH stretch, 3240 cm^{-1}; C≡N stretch, 2190 cm^{-1}). In another experiment, the condensate was collected at 100°C and, after it was analyzed as described above, was found to be virtually pure (~ 98 percent) urea (C=O stretch, 1640 cm^{-1}; NH_2 bend, 1600 cm^{-1}; NH_2 stretch, 3450 and 3350 cm^{-1}) (*20*).

The reduction of NO with CO and H_2 over Pt/Al_2O_3 was also investigated. The PTX-3 catalyst was used at a flow rate of 8.2×10^4 ml/hour per square meter of Pt surface area in the sample. The standard mixture was used at temperatures up to 500°C. No formation of NH_4OCN was detected, corresponding to a yield of less than 0.1 percent. The 0.5 percent Pt/Al_2O_3 catalyst, used with a flow of the standard mixture of 150 ml/min per gram of catalyst, gave yields of 0.4 and 0.6 percent NH_4OCN at 500° and 600°C, respectively. No NH_4OCN was detected at lower catalyst temperatures. Over both catalysts, NO was predominantly converted into NH_3.

Discussion. The implications of these results for the recovery of fixed nitrogen from dilute streams containing NO may be very significant. At present, most industrial nitrogen fixation is carried out by the Haber synthesis of NH_3. The NH_3 is then converted to NO by oxidation or to urea by reaction with CO_2 under high pressure. Alternative processes yielding NO, such as the thermal combination of N_2 and O_2 [Wisconsin process (*21*)] or various electrical arc and plasma processes (*22*), are not competitive, in large measure because of the difficulty of recovering NO from the dilute streams (1 to 2 percent) by adsorption or oxidation and absorption (*21*). The conversion of NO into NH_4OCN by the process described here, in the presence of O_2 or H_2 if required and at low pressure, may provide a competitive route to NH_4OCN and urea. It is anticipated that its economic feasibility may depend strongly on the "cost" of NO.

The implications of these results for the control of automotive emissions of NO by reduction of NO with CO and H_2 are of much interest also. These data (for instance, the fourth experiment in Table 1) show that under conditions that are similar to those in automotive exhaust a large fraction of NO may be converted to NH_4OCN, with NH_4OCN levels in the effluent from an unsupported Pt catalyst operating at 300° to 400°C approaching the levels of NO entering the catalyst. Water, O_2, and SO_2, which were found to be rather effective inhibitors for the formation of HCN (*2*, *23*, *24*), appear less effective in inhibiting NH_4OCN formation. Of course, in automotive exhaust control applications supported Pt and Pt-Rh catalysts are being used, and formation of NH_4OCN may be suppressed on

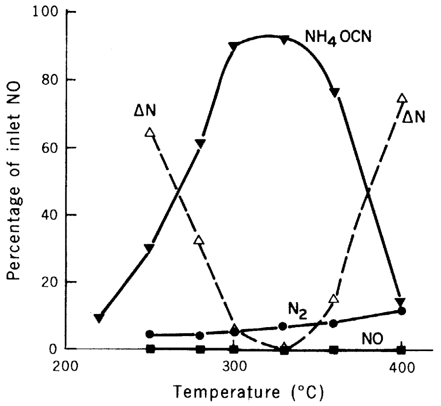

Fig. 2. Formation of NH_4OCN and N_2 in the reduction of NO with H_2 and CO over an Rh sponge catalyst (surface area, 1.69 m^2/g). The flow rate was 5.4×10^3 ml/hour per square meter of Rh surface in the sample. The standard gas mixture used is given in the legend of Fig. 1. Rhodium was reduced before use for 100 minutes at 500°C in pure H_2. The dashed line is explained in the legend of Fig. 1.

them as it was on the supported Pt catalysts included in this study. The differences between the conditions in our steady-state bench-scale experiments and the rapidly varying conditions in automotive exhaust make it impossible to say whether NH_4OCN will be formed to a significant extent when automotive exhaust is converted over Pt or Rh catalysts.

The results reported here enlighten the discussion (*4-12*) of whether OCN groups at the surface of metal catalysts could be important as intermediates in the formation of NH_3. The results show that NO is being converted to NH_4OCN over Pt and Rh catalysts of low surface area, but that hydrolysis of the cyanate over these metallic catalysts is slow near the temperature optimal for NH_4OCN production. They also show that on supported catalysts only a small amount of NH_4OCN is formed. Earlier workers have shown that NCO groups are formed on Pt and other metals (*5*) and may migrate to the oxidic support (*12*). The temperature dependence of the formation of NCO on the surface of Pt catalysts as measured by IR absorption (*9*) is similar (*19*) to the pattern of NH_4OCN formation in Fig. 1 and to the temperature dependence of NH_3 formation [figure 2 in (*25*)]. It therefore seems entirely reasonable to assume that hydrolysis of NCO groups to NH_3 occurs on the Al_2O_3 supports after their formation on the metal surface (*26*). We have also found that on Pt-Rh alloys, hydrolysis of NH_4OCN may be sufficiently fast at low temperatures to account for the formation of NH_3, whereas at higher temperatures hydrogenation of NH_4OCN is an important route to NH_3 (*19*).

For Ru, the variations with temperature of the surface concentration of NCO (*11*), of the formation of NH_4OCN (this work), and of the "CO-assisted" formation of NH_3 (*14*) are also very similar in the low-temperature regime. Since the maximal conversion of NO to NH_4OCN is 10 percent, compared to an NH_3 yield of 50 percent on unsupported Ru at the same temperature, hydrolysis of NCO to NH_3 appears in this case to be fast at the metal surface itself, in accord with the oxidic nature of the Ru surface (*27*).

In summary, we have established that NH_4OCN is a major product of the reduction of NO with CO and H_2, even in the presence of H_2O and O_2, over unsupported Pt and Rh catalysts in the temperature range 300° to 500°C. Almost quantitative conversion of NO to NH_4OCN ($\sim$ 95 percent) has been achieved. These results may lead to an alternative process for fixation of nitrogen as urea. They also have implications for the control of NO in automotive exhaust and for the mechanism of the formation of NH_3 in the reduction of NO.

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Hydrogen Cyanide Production During Reduction of Nitric Oxide over Platinum Catalysts: Transient Effects

Abstract. *The formation of hydrogen cyanide during the catalytic reduction of nitric oxide (NO) with carbon monoxide and hydrogen was studied with a bench-scale flow reactor. The previously reported inhibition by sulfur dioxide of the formation of hydrogen cyanide was found to be counteracted by transient admission of oxygen to the catalyst. These results are discussed in the context of the control of automotive emissions of NO and the prevention of hydrogen cyanide production during such control.*

We recently reported the production of HCN during the reduction of NO with CO and H_2 over Pt catalysts (*1*) and over other noble metal and base metal catalysts (*2*). Since the concentrations of NO, CO, H_2, and H_2O employed (0.3, 5, 0.5, and 3.5 percent, respectively) were similar to those found in automotive exhaust, we stated that "HCN formation over Pt under *reducing* conditions appears possible" in automotive catalytic exhaust systems when there is a low air/fuel ratio (*1*). Subsequent studies in the Environmental Protection Agency (EPA) by Bradow and Stump (*3*) confirmed the production of significant levels of HCN over Pt-Rh and Pt-Pd automotive catalysts. Regulations issued by the EPA require that HCN formation in vehicles must now be monitored for certification purposes (*4*). However, in the automotive tests HCN was formed in the