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The Formation of Compounds with the C≡N Bond During Reduction of NO Over Rhodium and Platinum Catalysts

The formation of HCN during the reduction of NO with H_2 and CO (*1*, *2*) has been the subject of recent regulations mandating the monitoring of HCN for certification of vehicles employing catalytic treatment of automotive exhaust (*3*, *4*). Study of the various products of reduction of NO is also of interest because it affords an insight into the chemistry of metal surfaces in contact with NO, CO, and other atmospheric pollutants which can and do combine to produce corrosive surface layers (*5*). The present note extends our earlier studies of the formation of HCN over Pt catalysts (*1*, *2*). The effect of the oxygen content of the inlet gas on the formation of HCN was studied. Simultaneously, the possibility of the formation of NH_4OCN over Pt was investigated. Finally, the formation of HCN over Rh was explored in view of the emerging importance of Rh as a reduction catalyst for NO (*6*, *7*).

The Pt catalyst used was a "sponge" (99.99% Pt, Engelhard Industries) with a surface area of 0.12 m^2/g. The Rh catalyst was a sponge (United Minerals and Chemical Co.) with a surface area of 1.69 m^2/g. The surface areas were determined with a Perkin–Elmer Sorptionmeter. The catalysts were in some cases diluted with α-Al_2O_3 chips of very low surface area. The catalyst (1–3 cm^3) is supported on a fritted quartz plate in a tubular quartz reactor. The details of the apparatus and the gas chromatographic analysis for NO, N_2, N_2O, CO, CO_2, and H_2 were the same as those reported in our earlier work (*1*, *2*) and have been described previously (*8*). A He diluent was employed in the gas entering the reactor, so that N_2 produced could be measured quantitatively by gas chromatography. Materials in contact with the effluent from the reactor were limited to quartz, type 304 stainless steel, and silver to prevent reaction of product compounds prior to analysis.

For the determination of NH_4OCN, we employed continuous scrubbing of 75 ml/min of gaseous reactor effluent with approximately 0.5 ml/min of an alcohol solution in a thin film absorber, followed by on-line and quantitative conversion of NH_4OCN in the solution into urea and colorimetric determination of urea as the yellow complex with diacetyl monoxime (*9*). This method has a sensitivity of 0.4 ppm of NH_4OCN in the gas phase and a relative error of $\pm 2\%$. A more detailed description will be published (*10*).

On-line analysis for HCN and NH_3 in the gas phase was carried out by using a discretely tuned CO laser-based opto-acoustic technique (*2*). The technique was modified to include determination of NO_2 by making measurements on five transitions of the carbon monoxide laser. In addition, the CO laser line utilized for NH_3 measurements was changed from that used in our earlier studies to avoid a possible interference from NO_2. The use of a new design of the opto-acoustic cell (*11*) required less time for a set of measurements which determines the

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TABLE 1

List of CO Laser Lines and Their Frequencies and Opto-Acoustic Signal on Each of the Laser Lines for Calibration Samples of HCN (1000 ppm), NH_3 (1000 ppm), NO_2 (100 ppm), and H_2O (10,000 ppm) in Helium[a]

CO laser		Opto-acoustic signal			
Line	Frequency (cm^{-1})	1000 ppm HCN	10000 ppm H_2O	100 ppm NO_2	1000 ppm NH_3
$P_{27-26}(12)$	1442.15	50	$<10^{-3}$	$<10^{-4}$	$<10^{-4}$
$P_{24-23}(15)$	1504.24	$<10^{-5}$	11.8	$<10^{-5}$	$<10^{-5}$
$P_{20-19}(20)$	1582.86	$<10^{-5}$	$<10^{-2}$	16.3	$<10^{-3}$
$P_{15-14}(14)$	1729.06	$<10^{-5}$	$<10^{-2}$	$<10^{-4}$	32

[a] The opto-acoustic signal was normalized to laser power. The total gas pressure in the opto-acoustic cell was 30 Torr.

concentration of HCN, NH_3, NO_2, and H_2O simultaneously in the effluent. The increased speed of the measurements recently allowed determinations of HCN and NH_3 under transient conditions (*12*). Table 1 specifies the CO laser lines used for the opto-acoustic absorption measurements and the opto-acoustic signal observed with calibration samples of HCN, NH_3, NO_2, and H_2O. Table 2 gives the interference-limited detection abilities for the gases. The details of the measurement technique will be described in the future (*13*). The effluent from the reactor was continuously sampled through the opto-acoustic absorption cell with an average residence time in the cell of less than approximately 10 sec. Factors limiting the rapidity of the measurements are the total volume of gas in the transfer lines and delays associated with absorption or desorption of the gases (to be measured) in various transfer lines.

TABLE 2

Interference-Limited Measurement Capability for Detection of HCN, NH_3, NO_2, and H_2O in the Reactor Effluent[a]

	HCN	NH_3	NO_2	H_2O
Interference-limited measurement capability	0.5 ppm	0.5 ppm	0.2 ppb	1 ppm

[a] The total gas pressure in the opto-acoustic cell was 30 Torr.

In general, at high concentrations of HCN and NH_3 the determination of the particular species takes a few seconds. In the region of 1 ppm of HCN total time for obtaining HCN measurements was approximately 1 min.

Prior to studying the effect of O_2 on the formation of HCN over Pt, the earlier data (*1*, *2*) on the temperature dependence of the formation in a mixture of 0.3% NO, 0.5% H_2, and 5% CO in He (the "standard mixture") were reproduced. It was noted that without the dilution of the Pt sponge with Al_2O_3 chips, the peak in the formation of HCN occurred at somewhat higher temperatures (725–750°C) and the peak level of HCN in the effluent was 300 ppm (as compared with 710°C and 400 ppm, respectively, in the presence of α-Al_2O_3). The α-Al_2O_3 chips alone were inert with respect to the gas mixture.

The effect of O_2 on the formation of HCN and NH_3 was studied at various temperatures with 0 to 2.2% O_2 added to the standard mixture of NO, CO, and H_2 in He. The yield of NH_4OCN was measured concurrently. The results are shown in Figs. 1 and 2 for 652 and 726°C, respectively. No α-Al_2O_3 dilution was used for these experiments. In the presence of H_2O in the standard mixture, HCN formation was depressed substantially, as reported previously (*2*). In experiments over "sponge" Pt diluted with α-Al_2O_3 at 697°C, 345 ppm HCN was found in the converted standard mixture, and this decreased to 37 ppm by adding 4.6% H_2O to the inlet gas. Addition of 2% O_2 to this wet inlet gas further decreased the yield of HCN to about 7 ppm (Fig. 3). No analysis of NH_4OCN was made for these experiments.

The yield of HCN over sponge Rh diluted with α-Al_2O_3 showed substantial variability dependent on the pretreatment and history of the catalyst. Four series of experiments were performed, with prereduction of the Rh at 450, 500, or 600°C, respectively, all at a flow rate of 62 liters/h per m^2 of Rh surface. In each case the temperature dependence was measured from low to high temperature, taking about one data point per 0.5 h after steady state conditions appeared to have been reached. After reaching 740 to 760°C, the HCN formation was substantially reduced upon returning to lower temperatures. Heating the catalyst at 450°C in 2% H_2 for 2 days, however, again increased the yield, with a different temperature dependence of the yield. Levels of between 5 and 60 to 100 ppm of HCN were found at any temperature from 500 to 750°C, but the results were very dependent on the history of the Rh catalyst. Because of the extreme variability of the characteristics of Rh in this reaction (unlike Pt), the study was not pursued further, since the HCN yield on Rh is likely to be very dependent on the details of the state of the catalyst as used in catalytic control systems.

Our study of the reduction of NO over Pt catalysts has shown that the reduction

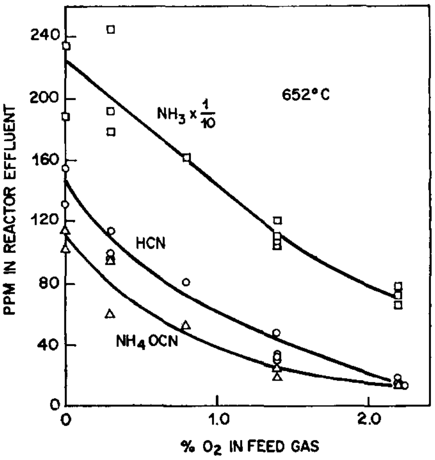

FIG. 1. Concentrations of NH_3, HCN, and NH_4OCN in effluent from reduction of NO over Pt sponge catalyst. Inlet gas: 0.3% NO, 0.5% H_2, 5% CO, and variable O_2 in He. Flow rate: 7×10^4 ml/h per m^2 of Pt surface. Temperature of Pt: 652°C.

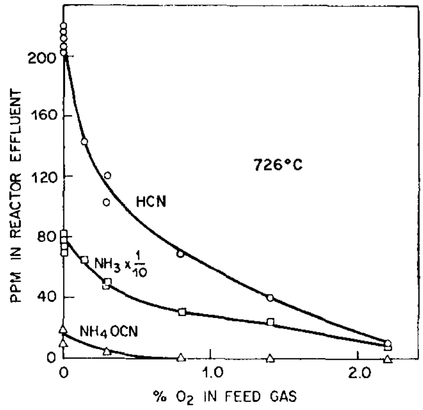

FIG. 2. Concentrations of NH_3, HCN, and NH_4OCN in effluent from reduction of NO over Pt sponge catalyst. Gas flow and composition are the same as those given in the legend to Fig. 1. Temperature of Pt: 726°C.

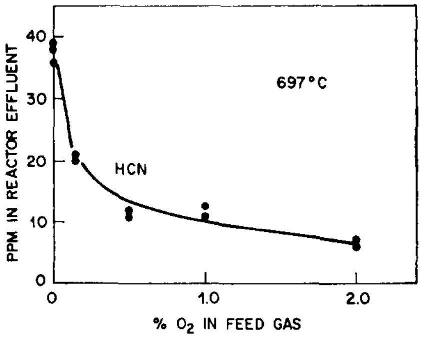

FIG. 3. Concentrations of HCN in wet effluent from reduction of NO over Pt sponge catalyst. Inlet gas: 4.6% H_2O, 0.3% NO, 0.5% H_2, 5% CO, and variable O_2 in He. Flow rate: 7×10^4 ml/h per m^2 of Pt surface. Temperature of Pt: 697°C.

products in dry mixtures at temperatures of 650 to 800°C are, in addition to N_2 and in order of decreasing preponderance, NH_3, HCN, and NH_4OCN. The yields of the last three products decreased progressively with increasing O_2 content in the inlet gas. To our knowledge, this is the first time that NH_4OCN has been found in the effluent from the reduction of NO over Pt catalysts. The formation of NH_4OCN at these high temperatures suggests that NCO adsorbates found at low temperatures [400°C, Ref. (*14*)] are relatively stable even as high as 700°C and are possible intermediates in the formation of HCN. There is no evidence in these data for oxidation of CN to OCN groups, a reaction which has been found to occur under different conditions (*15*). The yields of HCN from Rh sponge were found to be less than on Pt, but due to the extreme variation of the yield over Rh with seemingly minor differences in history of the catalyst, no definitive ranking of Rh as a HCN producer is warranted. It should be noted that studies of HCN formation in automotive exhausts have indicated that catalysts containing Rh/Pt alloys are more likely to produce HCN than Pt alone (*3*, *4*).

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R. J. H. VOORHOEVE
C. K. N. PATEL
L. E. TRIMBLE
R. J. KERL

Bell Laboratories
Murray Hill, New Jersey 07974

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