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The formation of isocyanic acid during the reaction of NH_3 with NO and excess CO over silica-supported platinum, palladium, and rhodium

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Abstract

The reaction between NH_3 and NO in excess CO over silica-supported platinum, palladium, and rhodium has been investigated for temperatures from 100 to 450 °C. As found previously for the corresponding reactions of H_2/NO/CO mixtures, isocyanic acid (HNCO) is produced with each catalyst. With Pd/SiO_2, the peak yield when NH_3 is used is 46% based on the total nitrogen converted and 55% based on the hydrogen taken from NH_3, with the remaining hydrogen converted to water. The reaction over Pt/SiO_2 requires a somewhat higher temperature and is more efficient with a maximum HNCO yield of 70% based on nitrogen and 95% on hydrogen. The near-absence of water as a product correlates with the high activity of platinum for the production of HNCO from H_2O/NO/CO mixtures, which in turn is driven by activity for the water–gas shift reaction. The peak yield of HNCO from NH_3/NO/CO mixtures is much lower with Rh/SiO_2 (10% based on nitrogen), and, unlike the yield of the platinum and the palladium catalysts, it is less than that observed during the $H_2 + NO + CO$ reaction (30%). In experiments using ^{15}NO and $^{14}NH_3$, the ^{15}N content of N_2, HNCO, and the end nitrogen of N_2O are similar, consistent with dissociation of both nitric oxide and ammonia to form a single surface pool of nitrogen atoms. However, neither dissociation is rapidly reversible, since there is little exchange of ^{14}N from ammonia into unreacted ^{15}NO, and significant formation of $^{15}NH_3$ is confined to Pt/SiO_2 at temperatures where it could be formed by hydrolysis of product $H^{15}NCO$. It is concluded that HNCO is formed by the rapid pick-up of surface hydrogen atoms by metal-bound NCO groups existing in equilibrium with N atoms and surrounding CO molecules. The trends in product distribution and in activity between the three metals can be rationalised in terms of competition between NO and CO for surface sites with CO favoured on Pt, NO favoured on Rh, and Pd exhibiting intermediate characteristics.

Keywords: NO reduction by NH_3 and CO; $NO + NH_3$; $NO + CO$; Isocyanic acid; HNCO; Pt/SiO_2; Rh/SiO_2; Pd/SiO_2; ^{15}N isotope

1. Introduction

In a rather remarkable series of four papers published in 1978, Voorhoeve and Trimble showed that cyanate compounds could be made in high yield by the reaction of H_2 and NO in a large excess of CO over unsupported platinum-group metal sponges [1–4]. When Pt and Rh were used, up to 98% of the NO in the feed could be converted to solid ammonium cyanate (NH_4OCN), which isomerised to urea when collected above 60 °C [1,3]. With Pd and Ir the major product was gaseous isocyanic acid (HNCO) [2,4]. Only one type of supported catalyst, Pt/Al_2O_3, was tested. No cyanates were seen in the products. Instead the major nitrogen-containing product was ammonia, which was attributed to the hydrolysis of NCO groups that form on platinum and then migrate to alumina [1]. Hecker and Bell subsequently reported that urea was produced during the reaction of H_2, NO, and CO mixtures over a reduced rhodium on silica catalyst [5]. They suspected, but were unable to prove, that isocyanic acid was formed when the catalyst was pre-oxidised but lost within their system, possibly as its non-volatile trimer, cyanuric acid.

In 1996 we used on-line FTIR analyses to show that gaseous isocyanic acid is a primary product of the reaction of H_2, NO, and CO over a Pt/SiO_2 catalyst [6,7]. The for-

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mation of solid deposits was avoided altogether because the reactor, infrared cell, and all connecting tubing were maintained above 90 °C. The stoichiometry of HNCO formation appeared to be best described by the equation

$$NO + CO + 1.5H_2 \rightarrow HNCO + H_2O. \tag{1}$$

This could be rationalised in terms of existing knowledge concerning NO dissociation and the hydrogenation of metal-bound NCO groups. If Al_2O_3 was placed downstream of Pt/SiO_2, or if Pt/Al_2O_3 was used instead of Pt/SiO_2, then all HNCO was hydrolysed to ammonia and carbon dioxide:

$$HNCO + H_2O \rightarrow NH_3 + CO_2. \tag{2}$$

In subsequent work, we used an improved version of this system to examine HNCO formation from H_2, NO, CO mixtures over silica-supported Pt, Pd, and Rh [8,9]. Yields of HNCO were low with Rh/SiO_2, but Pd/SiO_2 was almost as effective as Pt/SiO_2. The data for the latter two catalysts also suggested that HNCO could be formed not only from hydrogen but also in a second stage in which ammonia, initially produced in parallel with HNCO by the $NO + H_2$ reaction, was itself converted to HNCO. In a recent publication we reported that HNCO can indeed be produced in this way from substoichiometric amounts of NH_3 in mixtures of NO and CO over both Pd/SiO_2 and Pt/SiO_2 catalysts [10]. It should be noted here that one of the papers of Voorhoeve and Trimble (and a patent) does include data showing that the addition of NH_3 to H_2, NO, CO or H_2O, NO, CO feeds increases the yield of ammonium cyanate over a platinum–10% rhodium sponge [4,11]. This was attributed to the scavenging of HNCO on the metal surface by ammonia, potentially allowing the production of 1 mole of NH_4OCN for each mole of NO reacted rather than the 0.5 mole of NH_4OCN possible if both nitrogen atoms in NH_4OCN must be supplied by NO. However, there was no suggestion that NH_3 could be converted to the NCO moiety itself, as indicated by our data for Pt/SiO_2 and Pd/SiO_2 [10].

The aim of the present work was to determine the characteristics of silica-supported Pt, Pd, and Rh for catalysis of the ternary mixture, NH_3 and NO in excess CO, in comparison with their characteristics for two binary reactions, $NO + NH_3$ and $NO + CO$. The third binary system, $NH_3 + CO$, can be disregarded under steady-state conditions since thermodynamically possible yields, to either $HNCO + H_2$ or $HCN + H_2O$, are negligible at the temperatures of interest here. The present measurements have been carried out with NH_3 in stoichiometric excess over NO to preserve reducing conditions at all NO conversions, and they include comparison with the H_2, NO, CO system with the same concentrations. Isotope labelling is used to assess whether the nitrogen atoms derived from the NO or NH_3 are selectively converted to particular nitrogen-containing products.

The findings are of interest in the context of three-way catalysis as applied to motor vehicles, where NO, CO, and NH_3 can all be present in the converter under some conditions. The possible emission of isocyanic acid itself is not an issue in those systems, since further hydrolysis to ammonia by reaction (2) is certain to be fast on alumina and ceria–zirconia washcoats [8,9], especially given the high concentration of water present. Nonetheless, ammonia itself is undesirable since it plays a role in the production of haze-causing particulates in urban atmospheres [12].

2. Experimental

The test system and the analytical methods used in the present work were as described in detail previously [8,9]. In essence, catalyst samples (75 mg) were held in 4-mm i.d. Pyrex tubes with a test stream of 100 cm^3(STP)/min passing down flow. The feed was made by blending gas mixtures (supplied by BOC, Australia), with the use of electronic flow meters, to nominal concentrations of 3400 ppm CO, 1000 ppm NO, and, if present, 1500 ppm H_2 or 1000 ppm NH_3. The exit gas was analysed by a combination of gas chromatography (with a MTI Instruments model 200 instrument) and on-line FTIR (with a 16-cm path-length cell held at 90 °C) with spectra acquired every 10 min (3 min for the isotope experiments) with the use of a Nicolet Magna 550 instrument accumulating 64 scans at 0.25 cm^{-1} resolution. The HNCO concentrations were obtained by correcting the absorbance at 2284 cm^{-1} for a small contribution from CO_2 and then using a calibration factor obtained previously [8].

The concentrations of CO_2, CO, NO, N_2O, NH_3, and H_2O were obtained by processing various regions of the spectra with the program MALT developed by Griffith [13], which incorporates a least-squares fit against a set of synthetic spectra generated from the HITRAN data base [14]. In principle this method is absolute and does not require calibration. The accuracy for CO, CO_2, NO, and N_2O was ±5% at worst based on standard gas mixtures. Accurate standards were not available for NH_3 or H_2O, and the fitting procedure was less certain because of the sharpness of their lines. As noted later, mass balance calculations suggest that the concentrations determined for both NH_3 and H_2O are likely to be high by about 10%.

The ^{15}NO (Isotec Inc.; nominally 99.6% ^{15}N but with $\sim 4\%$ $^{14}N^{16}O$ and 3.3% $^{15}N^{18}O$ as impurities) was made up in 1% Ar in helium and interchanged back and forth with an equal concentration of ^{14}NO in helium alone with the use of a $1/16''$ 4-port valve (Valco Inc.). A quadrupole mass spectrometer with multiple ion monitoring (Balzers Thermostar model GSD 300T) was used to follow the disappearance of ^{14}NO (at $m/z = 30$) and the appearance of Ar ($m/z = 40$), ^{15}NO (31), and nitrous oxides containing one and two ^{15}N atoms (45 and 46). $^{14}N^{15}N$ and $^{15}N_2$ could also be obtained from the signals at 29 and 30 after careful correction of signals for the contributions arising through fragmentation of the various nitrous oxides. Analysis for $^{14}N_2$ and $^{14}N_2O$ was not possible because of the dominant contributions of CO and CO_2 to signals at 28 and 44, respectively. The concentrations of all four nitrous oxides, $^{14}N_2O$, $^{14}N^{15}NO$, $^{15}N^{14}NO$,