

Oxidation of CO by NO over Rh(111)

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We have studied the oxidation of CO by NO over a Rh(111) catalyst at pressures between 2 and 120 Torr, paying particular attention to the nitrogen containing products. Reacting 8 Torr of CO with 8 Torr of NO at between 525 and 675 K, we detect three products, CO₂, N₂O, and N₂. All three products are formed with an apparent activation energy (E_a) near 33.5 kcal/mol. Within the range of temperatures and pressures we examined, N₂O is the primary N-containing product—Rh(111) is about 70% selective for N₂O. The selectivity for N₂O is insensitive to reaction temperature, reactant pressure, and NO conversion. By varying the reactant pressure at three different temperatures, we determined that the CO₂, N₂O, and N₂ production rates are all near zero order in both CO and NO pressure. The activation energies, reaction orders, and CO₂ production rates we observe are in good agreement with previously reported measurements over Rh(111). The major new result of our work is our finding that N₂O, not N₂, is the dominant nitrogen-containing product of the CO + NO reaction over a Rh(111) catalyst at temperatures below 650 K. © 1993 Academic Press, Inc.

1. INTRODUCTION

Rh is a vital component of current automotive catalytic converters in large part because of its superior activity for the reduction of nitrogen oxides (NO_x) to nitrogen (1–3). In order to comply with future emission standards which require lower NO_x emissions and greater catalyst durability, we must take the maximum advantage of Rh's unique activity as an automotive exhaust catalyst. As a part of our effort to utilize Rh more effectively and thus to improve catalyst performance, we have studied the kinetics for the CO + NO reaction over a Rh(111) single crystal at partial pressures comparable to those present in automotive exhaust systems. By studying such a well-defined model catalyst we are able to specify with a high degree of certainty the rates and product distributions for important probe reactions. In this paper we concentrate on the nitrogen containing products of the CO + NO reaction. Our goal is to answer a simple question: do single

crystals and supported catalysts have the same products for CO + NO under similar reaction conditions?

The oxidation of CO by NO has been studied previously on both supported Rh catalysts (4–8) and Rh single crystals (9–11). N₂O and N₂ were observed as products for the CO + NO reaction over both Rh/SiO₂ (4, 5) and Rh/Al₂O₃ (6–8) catalysts. However, when the CO + NO reaction was run over Rh single crystals, N₂O either was not observed (11) or was not directly monitored (9, 10). In this paper we show that both N₂O and N₂ are formed over Rh(111) in a manner that is very similar to that of a conventional Rh/SiO₂ catalyst (4, 5). The behavior of Rh/SiO₂ and Rh(111) catalysts appears to be different from that of Rh/Al₂O₃ automotive catalysts which form exclusively N₂ and no N₂O over a wide range of operating conditions (6–8, 12). However, this paper does not address the conditions, very high NO conversions and high reaction temperatures, where Rh/Al₂O₃ catalysts have the highest selectivity for N₂.

2. EXPERIMENTAL ASPECTS

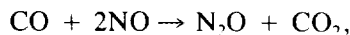
The experiments were performed in a custom built system which couples an ultrahigh vacuum (UHV) analysis chamber with a moderate pressure (≤ 200 Torr) reactor. The reactor and analysis chambers can be separated with a gate-valve. The UHV chamber is equipped with a wide array of analytical techniques. For this study we used low energy electron diffraction (LEED), X-ray photoelectron spectroscopy (XPS), and temperature programmed desorption (TPD). Preparation of the Rh(111) crystal and the details of our reactor and gas chromatograph (GC) apparatus are in a previous paper (13).

Reactions were done in a batch mode and the products and reactants were measured with a GC using a 6 ft \times $\frac{1}{8}$ in. stainless steel HAYESEP N column operated at 323 K with a He carrier gas. Column effluents were monitored using both a flame ionization detector (FID) and a thermal conductivity detector (TCD), which were in series. Gases first passed through the TCD, then through a methanizer with a Ni catalyst, and then to the FID. Using this arrangement we were able to detect NO (TCD), CO (TCD and FID), N₂O (TCD), and CO₂ (TCD and FID). N₂ was detectable with the TCD; however, our column did not separate N₂ from CO, making quantification of the amount of N₂ unreliable. However, by comparison of the TCD (CO + N₂) and FID (CO only) signals we could qualitatively observe N₂ as a product.

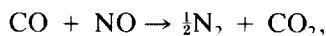
The CO₂ turnover numbers (TONs) were obtained directly from the calibrated GC measurements. Measurement of the N₂O TONs was complicated slightly by the presence of N₂O as a contaminant (about 0.5% N₂O) in the NO supply. We corrected the postreaction N₂O GC intensity by subtracting the previously measured contribution from N₂O in the NO supply. Measurements made using isotopically labeled N₂O and mass spectrometer detection showed that the N₂O in the NO supply does not react with CO in all temperature ranges of the

experiments. The correction for the N₂O in the NO supply becomes significant at NO pressures of about 40 Torr, where the amount of N₂O formed in the reaction is about equal to that present as a contaminant in the NO supply. Thus, for reactions using high NO pressures, the N₂O TONs are subject to about twice as much error as measurements made using 8 Torr of NO.

The N₂ TONs are estimated from the measured TONs for CO₂ and N₂O in conjunction with the known stoichiometries for N₂O formation,



and N₂ formation,



using

$$\text{N}_2 \text{ TON} = \frac{1}{2}[\text{CO}_2 \text{ TON} - \text{N}_2\text{O TON}].$$

The uncertainty in the N₂ TON is high relative to that for the CO₂ and N₂O TONs because it is obtained by subtraction of two very similar values. The error in the N₂ TON is largest for reactions using high NO pressures due to increased error in the N₂O TON (see above). We estimate that in the worst case the N₂ TON could be off by as much as a factor of 2.

The experimental procedure for making a rate measurement was as follows: (1) the reactants were leaked into the reactor, (2) the sample was ramped to the reaction temperature ($525 \text{ K} \leq T \leq 650 \text{ K}$) at 10 K/sec, (3) the timer was started when the sample was within 5° of the reaction temperature, (4) the temperature was held ($\pm 2^\circ$) for a specified time interval, (5) the sample was cooled to room temperature, and (6) after 5 min (waiting longer had no effect on the results) the gases in the reactor were expanded into an evacuated GC line. GC data were stored on our laboratory computer for analysis.

3. RESULTS

When CO and NO were reacted over Rh(111) three products were observed:

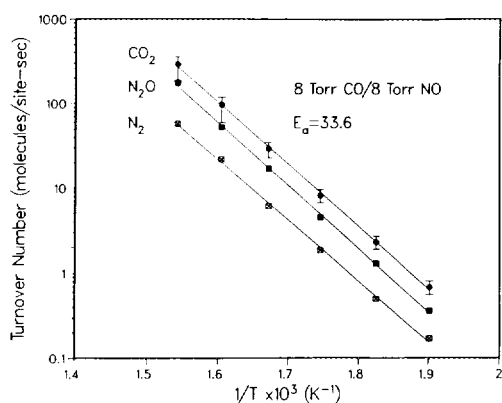


FIG. 1. Specific rates versus $1/T$ for the CO + NO reaction on Rh(111) measured using $P_{\text{CO}} = P_{\text{NO}} = 8$ Torr. The figure shows formation rates for the three products (CO_2 , N_2O , N_2) that we observed.

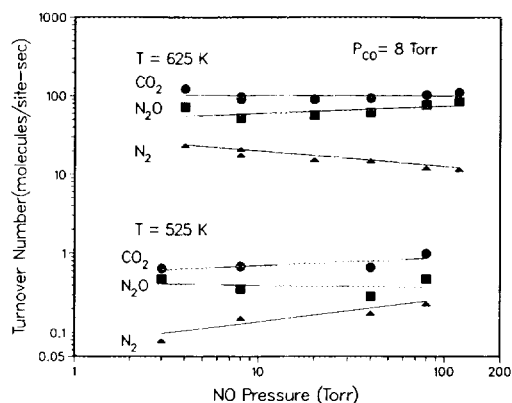


FIG. 2. The CO_2 , N_2O , and N_2 TONs versus P_{NO} with a fixed CO pressure of 8 Torr and reacting at two different temperatures (525 K and 625 K).

CO_2 , N_2 , and N_2O . Fig. 1 shows the TONs (symbols) for each product plotted vs $1/T$ for the reaction of 8 Torr CO and 8 Torr NO between 525 K and 650 K. The lines in Fig. 1 are linear least-squares fits of the data. Linear regression analysis gives the same (within experimental error) apparent activation energy (E_a) (≈ 33.5 kcal/mol) for the formation of all three products. The pre-exponential factor (ν) for CO_2 formation is estimated to be 6×10^{13} CO_2 site $^{-1}$ sec $^{-1}$. Temperature dependent data obtained for two other reactant mixtures (Table 1) show that

E_a is relatively insensitive to reactant pressure. We feel that the relatively low E_a for N_2 formation measured using 40 Torr NO is an experimental artifact arising from N_2O in the NO supply (see Sect. 2).

Figure 2 shows the CO_2 , N_2O , and N_2 TONs vs P_{NO} using 8 Torr of CO and two different temperatures (525 K and 625 K). Linear regression analysis of the data suggests that the reaction orders for CO_2 and N_2O production are very near zero (Table 2). We attribute the deviations from zero order kinetics observed for N_2 formation

TABLE I
Apparent Activation Energies: CO + NO over Rh(111)

P_{CO} (Torr)	P_{NO} (Torr)	CO_2 formation	N_2O formation	N_2 formation
8	8	$E_a = 33.6^a$ $\nu = 6.0 \times 10^{13}{}^b$	$E_a = 34.1$ $\nu = 5.3 \times 10^{13}{}^c$	$E_a = 32.8$ $\nu = 6.6 \times 10^{12}{}^d$
80	8	$E_a = 33.9$ $\nu = 6.4 \times 10^{13}$	$E_a = 34.0$ $\nu = 3.2 \times 10^{13}$	$E_a = 33.7$ $\nu = 1.4 \times 10^{13}$
8	40	$E_a = 32.3$ $\nu = 2.4 \times 10^{13}$	$E_a = 36.4$ $\nu = 4.1 \times 10^{14}$	$E_a = 27.9$ $\nu = 1.2 \times 10^{11}$

^a kcal/mol.

^b CO_2 molecules/Rh site-sec.

^c N_2O molecules/Rh site-sec.

^d N_2 molecules/Rh site-sec.

TABLE 2
Reaction Orders: CO + NO over Rh(111)

Temp (K)	m^a CO ₂ ^b	m N ₂ O ^c	m N ₂ ^d	n^a CO ₂ ^b	n N ₂ O ^c	n N ₂ ^d
525	0.10	-0.03	0.29	—	—	—
575	-0.04	0.00	-0.12	0.05	0.06	0.03
625	0.00	0.09	-0.20	—	—	—

^a Rate = $kP_{\text{NO}}^m P_{\text{CO}}^n$.

^b Reaction order for CO₂ formation.

^c Reaction order for N₂O formation.

^d Reaction order for N₂ formation.

(Table 2) to errors arising from our method of estimating N₂ TONs (see Sect. 2). The CO pressure dependence is examined in Fig. 3, where TONs for CO₂, N₂O, and N₂ are plotted vs P_{CO} with P_{NO} fixed at 8 Torr and temperature constant at 575 K. Again, the formation rate of all three products is independent of the reactant pressure suggesting near zero order kinetics (Table 2).

Figure 4 consolidates all of our data in a different manner by plotting the N₂O selectivity vs temperature for three different reactant mixtures (see figure caption). The N₂O selectivity is defined as

$$S_{\text{N}_2\text{O}} = \frac{\text{mol N}_2\text{O}}{[\text{mol N}_2\text{O} + \text{mol N}_2]}$$

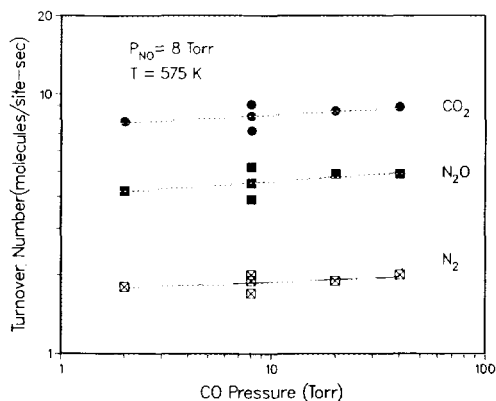


FIG. 3. TONs for CO₂, N₂O, and N₂ versus P_{CO} with P_{NO} fixed at 8 Torr and temperature constant at 575 K.

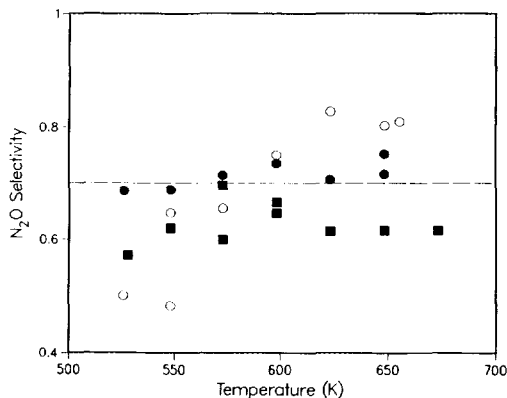


FIG. 4. N₂O selectivity versus temperature for three different reactant mixes: (●) 8 Torr CO/8 Torr NO, (■) 80 Torr CO/8 Torr NO, and (○) 8 Torr CO/40 Torr NO. The dashed line denotes 70% selectivity.

For the case with 40 Torr of NO the selectivity for N₂O appears to increase from 50% to 80% with increasing temperature. However, we attribute this trend to experimental errors arising from N₂O contamination in the NO supply (see Sect. 2). Examination of the two open circles at 550 K shows the high level of variation observed when high NO pressures were employed. We conclude that Fig. 4 shows that the reaction is roughly

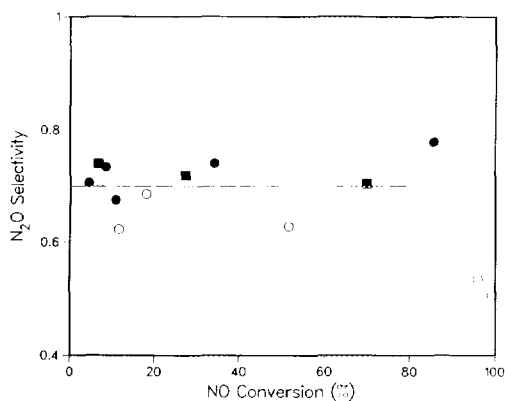


FIG. 5. N₂O selectivity versus NO conversion for reaction of (●) 8 Torr CO/8 Torr NO at 625 K, (■) 80 Torr CO/8 Torr NO at 625 K, and (○) 80 Torr CO/8 Torr NO at 650 K. The dashed line denotes 70% selectivity.

70% selective for N_2O over a wide range of temperatures and reactant pressures.

In Fig. 5 we examine the effect of NO conversion on the N_2O selectivity. Three different sets of reactant pressure and temperature were used for these experiments (see figure caption). The data (Fig. 5) show that the selectivity is insensitive to NO conversion. For only one condition, elevated temperature (650 K), high CO pressure (80 Torr), and 100% NO conversion, did the selectivity for N_2O change—it fell from 70% to about 50%.

4. DISCUSSION

4.1. *Rh(111) Reaction Products and Kinetics*

We reexamined the CO + NO reaction over Rh(111) because previous papers (9–11) suggested that N_2O was not a product over single crystals as it is for supported catalysts (4–8). To our knowledge two crystal faces have been previously examined. For reaction over Rh(100), N_2O either was not observed (11) or was not directly monitored (10). For reaction over Rh(111) (9, 10), N_2O was not directly monitored and therefore was not reported. We find that there are three products for the reaction of CO and NO over Rh(111). The products are CO_2 , N_2O , and N_2 . As for the nitrogen containing species, Figs. 4 and 5 show that over our range of temperatures, pressures, and conversions the reaction is roughly 70% selective for N_2O . In light of our results over Rh(111), we suspect that N_2O is also formed over Rh(100) and suggest that a reexamination of that surface would be useful.

4.2. *Comparison of Rh(111) and Supported Rh*

Our observation of N_2O formation for CO + NO over Rh(111) reconciles some of the previously reported differences between supported and single crystal Rh catalysts. In an early paper, Hecker and Bell (4) reported that N_2O is the major nitrogen containing product (about 80% N_2O) for CO + NO over a 5 wt% Rh/SiO₂ catalyst. Further, they re-

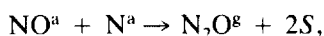
ported that the N_2O selectivity was relatively insensitive to reaction temperature and/or NO conversion. The behavior of Rh/SiO₂ catalysts is different from the currently accepted behavior of low loaded (≤ 0.1 wt%) Rh/Al₂O₃ (6–8). The Rh/Al₂O₃ catalysts show significant N_2O formation at low temperatures and/or NO conversions and almost exclusively N_2 formation at higher temperatures where the NO conversion is above 50% (6–8). In contrast to either of these supported catalysts, previous papers on single crystals left the impression that N_2O was not formed over single crystals (9–11).

Our results show that Rh(111)'s CO + NO activity is very similar to that observed for relatively large Rh particles on SiO₂ (4, 5). Both Rh(111) and Rh/SiO₂ have similar product distributions (more N_2O than N_2), reaction orders (near zero in P_{CO} and P_{NO}), and activation energies (33.5 Kcal above 480 K). We conclude that this behavior is the signature of bulk Rh activity for CO + NO. The bulk Rh activity that we observe appears to be different from the activity of low loaded Rh/Al₂O₃ catalysts. As stated above, over Rh/Al₂O₃ the N_2O selectivity is a strong function of reaction temperature and/or NO conversion (6–8). More recently, we have obtained results for a PtRh alloy single crystal, which suggest that this temperature dependence for the N_2O selectivity can also be found over bulk Rh catalysts. The major differences in the Rh/Al₂O₃ and bulk Rh catalysts appears to be the temperature and NO conversion levels at which the selectivity switches away from N_2O and towards N_2 . It is possible that these differences are not related to the reaction kinetics, but are more strongly influenced by heat and mass transfer differences between different types of catalysts. At this time, we are unable to make a strong statement as to how and why low-loaded Rh/Al₂O₃ catalysts appear different from Rh(111) catalysts.

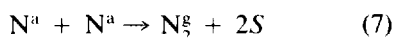
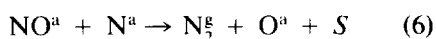
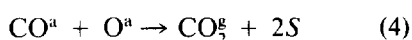
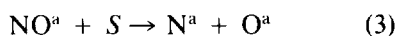
4.3. *Mechanism for CO + NO over Rh(111)*

Our results show that the previously proposed mechanism (9) for CO + NO over

Rh(111) must be modified to include N_2O formation. We propose that N_2O forms via



where superscript a denotes adsorbed and superscript g means gas phase. This step has been previously included in mechanisms for reaction over supported catalysts (4–8). Thus, for $CO + NO$ over Rh(111) we propose



At this time, we are making UHV measurements of the rate constants for steps (6) and (7). These measurements are required in order to model the reaction kinetics and thereby quantitatively assess the viability of this mechanism.

4.4. Reaction Kinetics over Rh(111)

Any model of the reaction kinetics for $CO + NO$ over Rh(111) must be consistent with the central result of this work: the remarkable insensitivity of the N_2O selectivity to reaction conditions. More specifically, we observe that (1) the N_2O selectivity is generally insensitive to temperature between 525 and 675 K, (2) the N_2O selectivity is insensitive to the conversion level of the reaction, (3) the N_2O , CO_2 , and N_2 formation rates are all near zero order in P_{CO} and P_{NO} , and (4) N_2O , CO_2 , and N_2 are formed with the same apparent activation energy.

Using our mechanism, the observed selectivities and apparent activation energies can be explained in two simple ways. One explanation is that step (7), N atom recombination, is slow. In this case, both N_2O and N_2 will form by a reaction that is first order in Θ_{NO} and Θ_N . Consequently, the N_2O se-

lectivity will not be affected by temperature or pressure induced changes in Θ_{NO} and Θ_N provided that steps (5) and (6) have similar activation energies. A simple way to rationalize this scenario is for N_2 and N_2O to have a common surface intermediate, say an “ N_2O -like” species, which could dissociate to form N_2 or desorb as N_2O . N_2 and N_2O will form with the same apparent activation energy if the important activation barrier is to the formation of this intermediate. A common intermediate of this type has been previously proposed to explain NO TPD data from Rh(111) (14).

A second probable reaction course is the following: N_2O is formed via step (5) and N_2 is formed via N atom recombination, step (7). The N_2O selectivity will be insensitive to reactant pressure only if Θ_{NO} and Θ_N are pressure independent. A further requirement is that any temperature dependent change in the Θ_N and Θ_{NO} must be balanced by differences in E_a for steps (5) and (7). Preliminary modeling suggests that these conditions can be fulfilled only if NO and N are *not* in direct competition for the same adsorption sites. This requirement seems reasonable since it is widely accepted that N atoms reside in the threefold hollow sites while NO adsorbs in the atop and bridging sites (15, 16). Modeling should allow us to make a definitive statement as to which is the more important pathway for N_2 formation under reaction conditions.

5. CONCLUSIONS

We have reexamined the reaction of NO and CO over a Rh(111) catalyst at pressures between 2 and 120 Torr because of our finding that N_2O is a major product of the reaction over Rh(111). Under our conditions (CO:NO pressure ratio between 10:1 and 1:5, $525 \text{ K} \geq T \leq 675 \text{ K}$) we find that the three products (CO_2 , N_2O , and N_2) are all formed with an apparent activation energy (E_a) near 33.5 kcal/mol. Over Rh(111), N_2O is the primary N-containing product—the reaction is about 70% selective for N_2O . The selectivity for N_2O is insensitive to reaction

temperature, overall conversion, and reactant pressure. By varying the reactant pressures we determined that the reaction rate is roughly zero order in both P_{CO} and P_{NO} . Our results indicate that the activity of Rh(III) very closely mimics that of conventional Rh/SiO₂ catalysts.

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