MECHANISM OF THE NITRIC OXIDE-CARBON MONOXIDE-OXYGEN REACTION OVER A SINGLE CRYSTAL RHODIUM CATALYST

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ABSTRACT

As part of a study of reactions important in automotive exhaust catalysis, the absolute rates of the CO-O₂ reaction over Rh(111) in the presence of NO have been measured and compared with the kinetics of the NO-CO and CO-O₂ reactions over Rh(111) at partial pressures relevant to automotive exhaust [8 Torr ≈ 0.01 atm]. At 550 K as sequentially larger amounts of NO are added to equimolar mixtures of CO and O₂ [P(CO) = P(O₂) = 8 Torr], we find that inhibition of the CO-O₂ reaction by NO is significant only when the NO pressure exceeds a level about one tenth of the equimolar pressures of CO and O₂. For a 1:1:1 NO:CO:O₂ mixture at 550 K, the CO₂ formation rate has dropped two orders of magnitude from the CO-O₂ rate without NO and, furthermore, has the same rate as the equimolar NO-CO mixture alone. UHV measurements of the low oxygen sticking coefficients on N atom-covered Rh single crystals suggest that the mechanism of NO inhibition of CO oxidation on Rh(111) is inhibition of oxygen adsorption by high nitrogen atom coverages.

INTRODUCTION

The reactions of CO with O₂ and NO over noble metal catalysts are important for the catalytic control of automotive exhaust emissions (1-4). Considerable attention has been focused on the kinetics and mechanisms of the CO-O₂ reaction (e.g., 4-9) and, to a lesser extent, the NO-CO reaction (e.g., 7-12), separately. Much less information is available for gas mixtures containing all three reactants, NO, CO, and O₂, which are more representative of automotive exhaust.

Rhodium has shown excellent activity both for CO oxidation [2CO + O₂ → 2CO₂] and NO reduction [2NO + CO → CO₂ + N₂] (1-4). Surface chemistry research on Rh single crystal surfaces to develop a better understanding of rhodium's catalytic activity has been carried out for several years (6,10,13-24). For example, the rate constants for all of the elementary steps of these reactions have been determined, such as NO dissociation [Eₗ = 19 ± 1 kcal/mole] (20) and CO desorption in the presence of N atoms (18). In addition, steady-state kinetic studies of both reactions have been carried out on Rh(111) and Rh(100) at low pressures [10⁻⁵⁻¹⁻⁷ Torr] (23-25)
as well as at higher, realistic pressures [1-300 Torr] (7-9) which include the partial pressure ranges of interest in the catalytic control of automobile exhaust emissions. Oh et al. (7) have compared these results over single crystals at realistic pressures with results obtained over supported Rh catalysts for the same reactions at the same temperatures and pressures. They find that rate expressions based on UHV-determined elementary intermediate steps using UHV-determined rate constants quantitatively predict the rates at high pressures for both the CO-O_2 and NO-CO reactions over single crystal Rh and supported Rh catalysts (7). The success of these predictions based on UHV work shows, for this important class of reactions, that the strongly-bound species present under the conditions of UHV studies are the same species reacting at high pressures. This success also encourages us to try to understand the more complicated reaction with NO, CO, and O_2 together using results obtained in ultrahigh vacuum studies.

One way to examine the interaction of NO, CO, and O_2 reactants on Rh is to investigate how the rate of the CO-O_2 reaction is affected by the presence of NO. In a kinetic study with a Rh/Al_2O_3 catalyst, Oh and Carpenter (26) have shown that NO has a strong effect in retarding the CO-O_2 reaction rate. They attribute the drop in the CO oxidation rate to the blocking of reactive sites by adsorbed NO. It is of interest then to explore what the effect of NO on the CO-O_2 reaction rate would be over a Rh(111) catalyst. Indeed, we find that NO strongly inhibits the CO-O_2 reaction over Rh(111) at realistic partial pressures of the gases. UHV studies indicated, however, that the mechanism of the CO-O_2 rate suppression by NO may be different on Rh(111) than on Rh/Al_2O_3. On Rh(111) oxygen adsorption appears to inhibit by the adsorbed nitrogen atoms and hence the CO-O_2 rate decreases dramatically.

EXPERIMENTAL

The apparatus used for the reactivity experiments is at Sandia National Laboratories and has been described in detail previously (27). Briefly, the system consists of an UHV surface analysis chamber connected to a high-pressure reaction chamber. The Rh(111) single crystal sample, mounted on the arm of a retractable bellows, can be transferred in vacuum from the reactor to the analysis chamber. The Rh(111) crystal is elliptically shaped measuring 0.91 by 0.58 cm and 0.09 cm thick and was heated resistively by two high-purity 0.020" tungsten leads spot-welded to the rear of the crystal. The temperature measurement was made by chromel-alumel thermocouples spot-welded to the edge of the crystal.

Auger electron spectroscopy (AES) was used to characterise the crystal surfaces before and after high-pressure reaction to insure atomic cleanliness before reaction and to investigate the chemical nature of the surface as a function of variable reaction conditions. Clean Rh surfaces could be conveniently obtained by running a CO-O_2 reaction in the high-pressure reactor, with any residual oxygen removed by heating the crystal to 1200 K in vacuum. Gas chromatography with flame ionization detection (FID) was used for the analysis of CO and CO_2, which were catalytically converted to methane before detection. Rates of "reaction" are expressed in units of turn-over number (TON) defined as the number of CO_2 molecules formed per surface metal atom per second. The number of surface Rh atoms in the sample was determined from the measured area of the crystal and the known atomic density of the Rh(111) surface, 1.6 x 10^16 atoms/cm² (10).

A typical experiment proceeded in the following manner: [1] the Rh surface was cleaned and checked by AES; [2] the sample was retracted and isolated from the UHV analysis chamber; [3] the reaction gases were introduced into the reaction chamber to the desired levels; [4] the sample
was resistively heated to the reaction temperature for a specified time with reaction terminated by quenching the crystal, i.e., the reactions were done in batch mode; [5] the reactant and product gases were allowed to equilibrate for approximately 15 minutes before small aliquots were injected into the gas chromatograph; [6] the reactor was evacuated and the sample reintroduced into the analysis chamber; [7] the sample was heated to at least 500 K to remove residual CO and NO (which will decompose in the electron beam of the Auger analyzer) before AES spectra were again obtained.

Pure $O_2$ (99.99%), NO (99.0%), and CO (99.99%) gases were used and the CO was further purified by passing the gas through a molecular sieve trap and a glass-wool trap both held at liquid nitrogen temperatures to remove volatile metal carboxyls. While only simple precautions were needed to remove Fe(CO)$_4$ from the CO, all of these measures were necessary to prevent Ni from Ni(CO)$_4$ from appearing on the sample after the reaction occurred. Post-reaction surface analysis as described above indicated the presence of only adsorbed nitrogen and oxygen atoms for reaction mixtures involving NO and a clean surface for near equimolar mixtures involving CO and $O_2$ alone.

In addition to the reactivity measurements discussed above, the oxygen adsorption studies were carried out using two ultrahigh vacuum systems at General Motors Research Laboratories which have also been described in detail elsewhere (18,28). Each system is equipped for multiplexed temperature programmed desorption (TPD), AES, and low energy electron diffraction (LEED), and has a typical base pressure of $3 \times 10^{-10}$ Torr ($= 4 \times 10^{-7}$ Pa). One system, in addition, contains the capability of X-ray and ultraviolet photoelectron spectroscopies (XPS, UPS), while the other has a high resolution electron energy loss spectrometer (EELS). Gases were usually admitted into the chamber through one of several capillary array dosers after positioning the sample within 3 mm in front of the doser. The crystals were heated resistively by passing current through two Ta wires spot-welded to the back of the crystal. A chromel-alumel thermocouple spot-welded to the top edge of the crystals was used to monitor sample temperatures. TPD spectra were collected while heating the crystal from 100 K to 1500 K at a rate of 10 K/s.

BACKGROUND RESULTS

The CO-$O_2$ Reaction

For the CO-$O_2$ reaction, we have measured the reaction rate over Rh(111) for a wide range of pressures around $P(CO) = P(O_2) = 8$ Torr, pressures similar to those found in automotive exhaust, and for temperatures between 450 K and 600 K (7-9). These data are shown in the upper part of Fig. 1. From 450 K to 800 K the reaction rate increases by almost four orders of magnitude and is characterized by a single

![Fig. 1. Specific rates over Rh(111) for the CO-$O_2$ and NO-CO reactions for equimolar mixtures of each reactant with reactant pressures of 8 Torr each.](image)
activation energy [29 kcal/mole]. The reaction is also first order in oxygen pressure and negative first order in CO pressure (7,9). We find excellent agreement between the specific rates and activation energies measured for a Rh(111) crystal and a 0.01 wt% Rh/Al₂O₃ catalyst, an indication of a structure-insensitive reaction.

The following elementary reaction steps were adopted to model the CO oxidation reaction at realistic pressures:

\[ \text{CO(g)} \rightarrow \text{CO(a)} \]  \hspace{1cm} (1)

\[ \text{O}_2(g) + 20(a) \]  \hspace{1cm} (2)

\[ \text{CO(a)} + 0(a) \rightarrow \text{CO}_2(g) \]  \hspace{1cm} (3)

Assuming steady-state reaction conditions, we can derive a rate expression for CO₂ formation which successfully predicts the measured absolute rates and activation energies. This expression uses only rate constants for the the four steps above which were determined experimentally in UHV studies for reactant coverages appropriate to reaction conditions [i.e., high CO coverage] (7). In fact, this same rate expression also predicts the CO-O₂ reaction rate at much lower pressures [~10⁻¹ Torr] and at lower temperatures [5400 K] where the CO coverage is approximately the same as that at high pressures (23). The picture of the CO-O₂ reaction confirmed by this work is that the Rh surface is predominantly covered by adsorbed CO with its coverage determined the adsorption-desorption equilibrium of CO [Eq. 1]. The reaction rate is limited by the adsorption of oxygen [Eq. 2] at the few remaining vacant sites.

The NO-CO Reaction

For the NO-CO reaction at realistic pressures over Rh(111), the reaction rate is positive order in NO pressure and zero order in CO pressure (7-9). From 500 K to 650 K the reaction has an apparent activation energy near 30 kcal/mole on Rh(111), as shown in the lower part of Fig. 1. After reaction the Rh(111) surface was found to be nearly covered with nitrogen atoms. The nitrogen atom coverage is also high near the rate maximum in low-pressure kinetic studies on Rh(111) (24).

The elementary steps shown below were used to model the NO-CO reaction:

\[ \text{CO(g)} \rightarrow \text{CO(a)} \]  \hspace{1cm} (4)

\[ \text{NO(g)} \rightarrow \text{NO(a)} \]  \hspace{1cm} (5)

\[ \text{NO(a)} + \text{N(a)} + \text{O(a)} \]  \hspace{1cm} (6)

\[ \text{CO(a)} + \text{O(a)} \rightarrow \text{CO}_2(a) \]  \hspace{1cm} (7)

\[ \text{NO(a)} + \text{N(a)} + \text{N}_2(g) + \text{O(a)} \]  \hspace{1cm} (8)

\[ 2\text{N(a)} \rightarrow \text{N}_2(g). \]  \hspace{1cm} (9)

Using a derived rate expression based on these steps for the NO-CO reaction, the observed absolute rates and activation energies at high pressures over Rh(111) were again correctly predicted using only UHV-determined elementary steps and rate constants (7). In the model, the overall reaction rate was found to be controlled by the availability of vacant sites. The concentration of such sites are, in turn, determined by the recombination of adsorbed nitrogen atoms and the subsequent desorption of N₂ [Eq. 9]. This behavior explained the lack of a dependence on CO pressure observed during high pressure reaction (7-9). That CO desorption does not limit the availability of vacant sites in the NO-CO reaction as it does in the CO-O₂ reaction can be attributed to the UHV-determined fact that the CO heat of adsorption in Eq. 4 is significantly reduced by coadsorbed nitrogen atoms (10).
In contrast with the structure insensitivity of the CO-O$_2$ reaction, the NO-CO reaction over Rh/Al$_2$O$_3$ has a lower rate and a higher activation energy [45 kcal/mole] (7) for a 1:1 NO:CO ratio than over single crystal catalysts. The complete behavior of the NO-CO reaction over Rh/Al$_2$O$_3$ can be successfully predicted, by assuming that the NO dissociation rate is about 2000 times slower on Rh/Al$_2$O$_3$ than on Rh single crystals (7). Finding the reason for the apparent difference in rate-limiting steps for the NO-CO reaction between bulk and supported Rh awaits further research.

RESULTS AND DISCUSSION

The NO-CO-O$_2$ Reaction

From our studies of the CO-O$_2$ and NO-CO reactions we were able to choose a temperature to begin our study of the NO-CO-O$_2$ reaction. As shown in Fig. 1, at 550 K for equimolar mixtures the specific rate of the CO-O$_2$ reaction is near 80 molecules/site-sec compared with about 0.8 molecules/site-sec for the NO-CO reaction. Since this was in the middle of an easily measurable range of rates, we added successively larger amounts of NO to equimolar mixtures of CO and O$_2$ [P(CO) = P(O$_2$) = 8 Torr] and measured rates at 550 K. As the results in Fig. 2 show, 0.01 Torr of NO has no effect on the CO$_2$ formation rate, but the rate drops steeply when the NO pressure is further increased to within a factor of 10 of the O$_2$ and CO pressures. An equimolar mixture of all three reactants has nearly the same rate as the NO-CO reaction alone at the same partial pressures. It appears that the 8 Torr of oxygen have very little effect on the NO-CO reaction.

To test whether we are observing more than just the inhibition of the CO-O$_2$ reaction, the NO pressure was increased further to 24 and 100 Torr. The rate then rose from its minimum rate measured at the 1:1:1 mixture and increased with increasing NO pressure. This behavior is very similar to that observed during the NO-CO reaction; that is, positive order in NO pressure at 500 K (7,9) for an equimolar mixture. For P$_{NO}$ ≥ 4 Torr we found considerable amounts of atomic nitrogen on the surface after reaction (29). This nitrogen could have been formed by dissociation during the heating.

![Diagram](image)

**Fig. 2.** CO$_2$ formation rate at 550 K over a Rh(111) catalyst for an equimolar mixture of CO and O$_2$ [P(CO) = P(O$_2$) = 8 Torr] with varying amounts of NO present.
step [#7] discussed in the Experimental section, but the surface N atom concentration increases with NO pressure well above the point where a monolayer of NO would be formed on the surface after reaction.

We believe that the data in Fig. 2 are best explained by assuming that the CO formed at low NO pressures \([P(\text{NO}) < 0.1 \text{Torr}]\) is a product of the CO-\(O_2\) reaction. Conversely, for high NO pressures \([P(\text{NO}) > 8 \text{Torr}]\) the CO is produced from the NO-CO reaction. At intermediate pressures both reactions are occurring, with the CO-\(O_2\) reaction becoming less dominant with increasing NO pressure.

Oxygen Sticking Coefficient with Adsorbed Nitrogen on Rh

While obtaining the UHV-determined rate constants used to successfully predict the CO-\(O_2\) and NO-CO reaction rates, we found that interactions between adsorbates often controlled the adsorption and desorption values we measured. For example, adsorbed nitrogen significantly decreases the heat of adsorption of CO explaining the zero order CO pressure dependence of the NO-CO reaction as discussed above. The role of N atoms should be important, since our results indicate that N atoms are present in significant amounts under reaction conditions on Rh(111) during the NO-CO reaction. In the model for this reaction which successfully predicts its high pressure rate, the dominant surface species is also N atoms. Hence, we have studied whether the presence of N atoms has any effect on the initial sticking coefficient for oxygen, \(S(O_2)\). By measuring the uptake of oxygen with temperature programmed desorption (TPD) and AES after a set of increasing exposures to oxygen, we find that \(S(O_2)\) for clean Rh(100) and Rh(111) is near unity at 100 K, and nearly the same at higher temperatures. However, with \(S_N\) near 0.5 on Rh(100), \(S(O_2)\) is less than 0.01, even at 100 K. These data suggest that N atoms may have a marked effect on oxygen adsorption at realistic pressures. This would be consistent with the apparent absence of CO oxidation by oxygen in the presence of P(\text{NO}) > 8 Torr in Fig. 2.

Another possible explanation is that adsorbed NO, rather than N atoms, inhibits oxygen adsorption. Under UHV conditions it is well-known that adsorbed NO will inhibit oxygen adsorption (19). However, under reaction conditions the same model that predicts the rate correctly, contains rate constants for NO dissociation which are high enough that there should be no large steady-state concentration of adsorbed NO under reaction conditions. So we may need to add to the UHV-determined parameters used to predict the CO-\(O_2\) and NO-CO reaction rates successfully. If we add a strong dependence of the initial oxygen sticking coefficient on nitrogen coverage, then we can predict the inhibition of the CO-\(O_2\) reaction rate in the presence of NO, without changing any rate constants.

If we compare the situation on alumina-supported rhodium with single crystal rhodium, the main difference, again based on the model calculation, is that the NO dissociation rate is about 2000 times slower on the supported catalyst. Hence, the NO (and CO) concentration may in fact be quite high on the support. Infrared studies during the NO-CO reaction show both species present, but NO is usually dominant (11,30,31). Adsorbed NO may be the main factor inhibiting oxygen adsorption in this case. Qualitatively the data over Rh/Al\(_2O_3\) for the NO-CO-\(O_2\) reaction are similar to that in Fig. 2, except that the CO production rate falls somewhat faster with increasing NO pressure than on Rh(111) (26). This would be consistent with adsorbed NO being the main inhibiting species on the supported catalyst.

CONCLUSIONS

We have examined the NO-CO-\(O_2\) reaction as a function of NO pressure over a Rh(111) catalyst at pressures pertinent to conditions during
automotive exhaust catalysis. We find that NO strongly inhibits the CO$_2$
formation rate when the NO pressure exceeds a value a factor of 10 less than
the CO and oxygen pressures. At 550 K an equimolar 1:1:1 NO:CO:O$_2$ mixture
has virtually the same rate as the NO-CO reaction, two orders of magnitude
less than the CO-O$_2$ reaction rate at the same temperature. We conclude that
CO is overwhelmingly being oxidized by NO (and not by O$_2$) in an equimolar
mixture. UHV studies of oxygen sticking on N atom-covered Rh single
crystals suggest that the CO-O$_2$ reaction is inhibited at high pressures by the
low oxygen adsorption rate in the presence of significant coverages of N
atoms derived from the dissociation of NO.

This work adds to our knowledge of the relative importance of the
elementary steps of the reactions involving CO, NO, and O$_2$ over Rh and
clarifies which steps need modification to increase overall reaction rates.
Further studies which can clarify the origin of the structure sensitivity of
the NO-CO and NO-CO-O$_2$ reactions over Rh would be most helpful. A more
complete understanding of both the CO oxidation and NO reduction reactions
will lead to the more effective use of rhodium in automotive exhaust
catalysis.

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