Evidence for structure sensitivity in the high pressure CO+NO reaction over Pd(111) and Pd(100)

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The chemisorption of coadsorbed CO and NO has been studied over Pd(111) and Pd(100) at 1 × 10^{-6} Torr using infrared reflection absorption spectroscopy. At a pressure ratio of PN0/P_CO = 1, the ratio of adsorbed NO to adsorbed CO, [NO]/[CO], increased with temperature over both single crystal surfaces. Furthermore, the [NO]/[CO] ratio was significantly higher on Pd(111) than on Pd(100) in the temperature range of 100–550 K, with NO being the predominant surface species above 400 K. The reaction of CO+NO to form CO_2, N_2O and N_2 was followed with infrared spectroscopy by monitoring the evolution of gas phase CO_2 and N_2O. At temperatures from 525–650 K, partial pressure ratios, P_NO/P_CO, from 16:1 to 1:16, and total pressures of 2–17 Torr, Pd(111) always showed higher activity than Pd(100) for both CO_2 and N_2O production. The Pd(100) surface, however, gave a higher branching ratio for N_2 versus N_2O production than Pd(111). The apparent activation energies of the reaction indicate a positive order in P_NO and a negative order in P_CO over both single crystal surfaces, with a zero order total pressure dependence between 2 and 20 Torr. The higher N_2/N_2O branching ratio observed on Pd(100) is likely due to the higher stability and surface coverage of dissociated nitrogen atoms on Pd(100) versus Pd(111), thus promoting the reaction 2N_2 → N_2. Both the higher activity and the higher selectivity for N_2O versus N_2 over Pd(111) are strongly correlated with the higher surface coverage of NO_2. In contrast, the lower activity of the Pd(100) surface relative to Pd(111) is likely due to enhanced poisoning of NO adsorption on this surface by dissociated nitrogen or oxygen atoms, or by adsorbed CO. © 1995 American Vacuum Society.

I. INTRODUCTION

Recently, there has been considerable interest in using palladium only catalysts for three-way exhaust gas conversion.1 Many ultrahigh vacuum (UHV) studies have focused on the nature of CO and NO chemisorption on low index planes of palladium.2 Much work has also been done to identify the CO+NO reaction products and kinetics over polycrystalline palladium surfaces.3–8 Few studies, however, have examined both the CO+NO reaction kinetics as well as the CO and NO coadsorbate coverages over well-defined surfaces at elevated pressures.3,9,10

In order to better understand the kinetics and mechanisms of the CO+NO reaction, it is essential to first identify the adsorption sites and surface coverages of the reactants. Many studies have been done to elucidate the structures of adsorbed CO and NO, separately, on well-defined palladium surfaces at UHV conditions.2 Few studies, however, have looked at the coadsorption of CO and NO on Pd at pressures higher than UHV.11,12

Several high pressure catalytic studies of the CO+NO reaction on Pd have observed significant production of gas phase N_2O, as well as N_2 and CO_2.4,13,14 Few studies, however, have considered the branching ratio between the optimum global reaction pathway

\[ \text{CO} + \text{NO} \rightarrow \text{CO}_2 + 1/2 \text{N}_2 \]  \hspace{1cm} (1)

and the less ideal pathway

\[ \text{CO} + 2 \text{NO} \rightarrow \text{CO}_2 + \text{N}_2 \text{O}. \]  \hspace{1cm} (2)

In this study, it will be shown that differences in the surface coverages of NO_2 on Pd(111) and Pd(100) are strongly correlated with different activities for CO+NO conversion, as well as different selectivities for N_2O versus N_2 production. The data presented in this article will provide conclusive evidence for the structure sensitivity of the CO+NO reaction over palladium.

II. EXPERIMENT

These experiments were performed in an ultrahigh vacuum chamber equipped with a Fourier transform infrared spectrometer for reflection absorption studies (IRAS), a mass spectrometer for temperature programmed desorption (TPD), an Auger electron spectrometer (AES) for monitoring surface cleanliness, and low energy electron diffraction (LEED) for determining surface order. The pressure in the infrared cell could be varied from 10^{-10} Torr to 1 atmosphere while maintaining ultrahigh vacuum in the main chamber.

The Pd(111) and Pd(100) substrates were cleaned in situ by repeated cycles of oxidation at 900 K followed by flash annealing to 1200 K. The surfaces were found to be free of oxygen and carbon contamination as measured by AES, and the surface orders corresponded well to their respective indices, as seen by LEED. Additionally, the surfaces were found to be free of active oxygen and carbon contamination by the absence of CO_2 in the TPD spectrum following CO adsorption and the absence of CO in the TPD spectrum following O_2 adsorption.

All gases used in the adsorption and catalytic experiments were obtained from Matheson and were of ultra-high purity.

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CO, CO$_2$ and N$_2$O were used as received. NO (C.P. grade) was subjected to repeated vacuum distillation cycles, using a liquid nitrogen-pentane bath to remove residual N$_2$O, NO$_2$ and CO impurities.

The CO+NO reaction was studied over Pd$_{111}$ and Pd$_{100}$ in a total pressure range of 2–17 Torr (batch mode), and a temperature range of 525–650 K. NO:CO pressure ratios were varied from 1:16 to 16:1, with the pressure of the minor component equal to 1 Torr. CO$_2$ and N$_2$O production was monitored with infrared spectroscopy. In these experiments, turnover frequency (TOF) is defined as the number of product molecules produced per surface site per second. Gas phase production of CO$_2$ and N$_2$O was calculated by converting infrared intensities to pressures using a set of calibration curves (partial pressure versus IR intensity). TOF’s were then calculated by normalizing the gas phase production of CO$_2$ and N$_2$O per second to the total number of surface sites.

III. RESULTS

A. CO+NO coadsorption

Figures 1 and 2 show the infrared reflection absorption spectra (IRAS) for the coadsorption of CO and NO on Pd(100) and Pd(111) as a function of temperature. The adsorbate layer was in equilibrium with an equimolar mixture of CO and NO at $1 \times 10^{-6}$ Torr. Adsorption spectra collected during cooling and warming of the surface showed the same frequencies and intensities, confirming reversibility in the coadsorption. Chemisorption experiments were carried out both before and after high pressure catalytic experiments to confirm that the adsorption sites and coverages had not changed. The reaction of CO and NO was negligible below 500 K over the time period of the adsorption experiment.

CO and NO coadsorbate bands have been assigned previously on Pd(100) and Pd(111) by comparing the IRAS spectra of coadsorbed CO and NO with the IRAS spectra of CO and NO adsorbed separately on these surfaces.$^{11}$ The cover- age ratio, $\frac{[\text{NO}]}{[\text{CO}]}$, can be estimated by comparing the integrated IR peak areas of CO and NO on similar adsorption sites. Fig. 3 shows the ratio of $\frac{[\text{NO}]}{[\text{CO}]}$ versus temperature over Pd(111) and Pd(100). The total surface coverage, $\theta$(total)=$\frac{[\text{NO}]}{[\text{CO}]}$, decreased as the temperature was increased, as seen by the lower intensities of the infrared bands at higher temperatures. On both surfaces, the ratio of

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**Fig. 1.** Infrared reflection absorption spectra of CO and NO coadsorbed on Pd(100). The crystal was in equilibrium with an equimolar ratio of CO and NO at $1 \times 10^{-6}$ Torr. Data were collected at the highest temperature first.

**Fig. 2.** IRAS spectra of an equimolar CO+NO mixture at $1 \times 10^{-6}$ Torr on Pd(111). The conditions were the same as in Fig. 1.

**Fig. 3.** Adsorbed NO/CO ratio, $\frac{[\text{NO}]}{[\text{CO}]}$, vs temperature over Pd(111) and Pd(100), estimated from the IRAS peak intensity ratios (line serves to guide the eye).
At all temperatures studied in this experiment, Pd~ showed about 7–10 times higher activity for CO₂ production than Pd~. Similarly, the pressure ratio, temperature range of 525–650 K. In Fig. 4, the gas phase intensity of CO₂ per second to the change in CO₂ pressure per second, and then normalizing to the number of surface sites.

\[
\text{[NO]}_a / \text{[CO]}_a \text{increased significantly at high temperatures and low total surface coverages. Based on the ratios of the infrared intensities, the approximate [NO]_a/[CO]_a on Pd(100) changed from about 1.5 at 100 K to about 1:1 at 400 K. Similarly, the [NO]_a/[CO]_a on Pd(111) ranged from about 1:2 at 100 K to about 10:1 at 450 K.}
\]

**B. CO+NO reaction**

Figure 4 shows the measured turnover frequencies (TOF's) for CO₂ production over Pd(111) and Pd(100) in the temperature range of 525–650 K. In Fig. 4, the gas phase pressure ratio, \( P_{\text{NO}} / P_{\text{CO}} \), was 1:1 and the total pressure was 2 Torr. At all temperatures studied in this experiment, Pd(111) showed about 7–10 times higher activity for CO₂ production than Pd(100).

Figure 5 shows the measured TOF's for N₂O production versus temperature over Pd(111) and Pd(100), measured concurrently with the CO₂ TOF's of Fig. 4. Again, Pd(111) gave a higher activity than Pd(100) for N₂O production. The differences in activities between the two surfaces for N₂O production, however, were somewhat larger than the differences for CO₂ production.

Although the total conversion of CO is accurately measured by the concentration of CO₂ formed, given that no catalyst coking occurred, the total conversion of NO is equal to the sum of the concentrations of N₂O and N₂ produced. Even though N₂ production cannot be measured directly with IR spectroscopy, the production of N₂ can be calculated by equating the two global reaction pathways (1) and (2). The total amount of CO₂ produced must equal the total amount of N₂O produced plus twice the total amount of N₂ produced. By mass balance of the products, we obtain

\[
[N_2]=\frac{1}{2}([CO_2]-[N_2O]).
\]

The validity of this equation is confirmed by the fact that no other measurable reactions occurred between CO and NO, as seen by the absence of additional peaks in the IR reaction spectra. Two types of blank experiments were performed, using IR spectroscopy and temperature programmed reaction spectroscopy (TPRS), to confirm that the CO+NO reaction over Pd was the only source of measured CO₂, N₂O and N₂. First, when either CO or NO was reacted separately over Pd, in the absence of the oxidant or reductant, no measurable reaction occurred. Also, when the Pd surface was coated with unreactive silica, the reaction between CO and NO under standard catalytic conditions was negligible.

Figure 6 shows the branching ratio between N₂O and N₂ production over Pd(111) and Pd(100) as a function of substrate temperature. This figure was obtained by comparing Fig. 5 (N₂O TOF's) with the calculated TOF's of N₂ obtained from Eq. (3). Under the reaction conditions, \( P_{\text{NO}} / P_{\text{CO}}=1 \) and \( P_{\text{total}}=2 \) Torr, the branching ratio of N₂O/N₂ was significantly higher over Pd(111) than Pd(100). The branching ratio of N₂O/N₂ also increased with temperature over Pd(111), whereas it remained relatively constant with respect to temperature on Pd(100). The higher N₂O/N₂ branching ratio over Pd(111) can be seen qualitatively by noting the larger differences in activities for N₂O production (Fig. 5) than for CO₂ production (Fig. 4) between the two surfaces.
The apparent activation energies \( E_A \)'s for the CO+NO reaction were calculated by using the Arrhenius equation, \( R = -E_A/RT \). Figure 7 shows the \( E_A \)'s for CO\(_2\) production over Pd(111) and Pd(100) versus \( P_{\text{NO}}/P_{\text{CO}} \) pressure ratio. At low \( P_{\text{NO}}/P_{\text{CO}} \) ratios (i.e., 1/16) the apparent \( E_A \) was about 25–30 kcal/mol, and at high \( P_{\text{NO}}/P_{\text{CO}} \) ratios (i.e., 16/1), the apparent \( E_A \) decreased to about 10–15 kcal/mol.

### IV. DISCUSSION

#### A. CO+NO coadsorption

The relative surface coverage ratios, \([\text{NO}]_a/[\text{CO}]_a\), shown in Fig. 3 can be estimated by comparing the intensities of the infrared bands of NO\(_a\) and CO\(_a\) on similar adsorption sites (i.e., atop, two-fold or three-fold). The infrared extinction coefficients for CO and NO adsorbed on similar surface sites are comparable, as seen by the equivalent integrated absorbances for the same saturation coverages. On Pd(100), the comparison between two-fold bridging CO and two-fold bridging NO is valid as this is the only adsorption site for these molecules. On Pd(111), comparison between three-fold CO and three-fold NO is also valid, as this is the main adsorption site at high temperatures.

At 450 K, the value obtained from the infrared intensity ratios of \([\text{NO}]_a/[\text{CO}]_a\) on Pd(111) is approximately 10:1, compared to approximately 1:1 on Pd(100). This value corresponds well with the estimated coverage ratio based on the ~2 kcal/mol higher heat of adsorption of NO on three-fold Pd vs CO on three-fold Pd.\(^{15}\) At lower temperatures (<200 K) on Pd(111), CO adsors on three-fold sites, whereas NO adsors in an atop configuration. Although these adsorption geometries are different, the \([\text{NO}]_a/[\text{CO}]_a\) is estimated to be about 1:2. This value is obtained by comparing the intensities of the infrared bands to the infrared intensities of CO and NO adsorbed separately at saturation coverage on Pd(111).\(^{16,17}\)

Qualitatively, IRAS measurements of CO+NO coadsorption at \( P_{\text{total}} = 2–20 \) Torr show similar trends to CO+NO coadsorption at \( 1 \times 10^{-6} \) Torr. Accurate measurements of re-actant coverages at reaction temperatures and pressures, however, are difficult because CO and NO are consumed rapidly by the reaction. Although the total coverage of CO and NO at reaction conditions is low, as seen by IRAS, NO\(_a\) is clearly more predominant on Pd(111) than on Pd(100).

Although the combination of effects responsible for the stabilization of NO\(_a\) relative to CO\(_2\) on Pd at high temperatures and low coverages is undetermined, the experimental data showing the predominance of NO\(_a\) is well established and reproducible. The IRAS data do not, however, provide conclusive support as to whether molecular NO is stabilized on Pd(111) relative to Pd(100) or if molecular NO is destabilized on Pd(100) due to surface poisoning. Additional evidence for surface poisoning on Pd(100) was seen in the NO TPD spectrum (not shown).\(^{18}\) A high temperature (700 K) nitrogen atom recombination peak was seen on Pd(100), but not on Pd(111). This highly stable \( N_a \) species (or perhaps an associated \( O_a \) species) is most likely responsible for poisoning NO adsorption and thus the CO+NO reaction on Pd(100).

#### B. CO+NO reaction

In order for the CO+NO reaction to proceed, NO must be adsorbed on the Pd surface in order to dissociate, since a bimolecular CO+NO reaction is unlikely. Figure 3 shows conclusively that the \([\text{NO}]_a/[\text{CO}]_a\) is higher on Pd(111) than on Pd(100) at all total surface coverages. Although the absolute surface coverages of NO\(_a\) and CO\(_a\) are unknown at reaction conditions, the higher \([\text{NO}]_a/[\text{CO}]_a\) on Pd(111) versus Pd(100) is strongly correlated with the higher activities for both CO\(_2\) and N\(_2\)O production (Figs. 4 and 5).

Figure 7 provides additional support for the importance of \( P_{\text{NO}} \) on the apparent activation energy, as well as the rate of the reaction. As the \( P_{\text{NO}}/P_{\text{CO}} \) is increased from 1:16 to 16:1, the apparent \( E_A \) decreases and the rates of CO\(_2\) and N\(_2\)O production increase over both surfaces. Separate IRAS experiments confirm that as the ratio of \( P_{\text{NO}}/P_{\text{CO}} \) is increased, the \([\text{NO}]_a/[\text{CO}]_a\) also increases. Figure 7 thus provides additional support for the activity of the CO+NO reaction being proportional to the \([\text{NO}]_a/[\text{CO}]_a\).

The effect of \( P_{\text{NO}} \) on catalytic activity is especially important for Pd(100), where it can be seen that the apparent \( E_A \) decreases to about 10–11 kcal/mol at \( P_{\text{NO}}/P_{\text{CO}} = 16:1 \), as opposed to about 16–17 kcal/mol on Pd(111). This result is consistent with an enhanced poisoning by \( N_a \) (or \( O_a \)) of NO adsorption on Pd(100) relative to Pd(111).

An additional consequence of the higher \([\text{NO}]_a/[\text{CO}]_a\) on Pd(111) is to increase the N\(_2\)O/N\(_2\) branching ratio (Fig. 6). At high \([\text{NO}]_a/[\text{CO}]_a\) ratios, reaction (2) is more favorable than reaction (1) because reaction (2) consumes more NO than reaction (1). On Pd(100), the \([\text{NO}]_a/[\text{CO}]_a\) never exceeds one when \( P_{\text{NO}}/P_{\text{CO}} = 1 \) (Fig. 3). Therefore, reaction (1), the 1:1 CO:NO stoichiometric reaction, is favored under all possible total surface coverages. Figure 6 also shows that as the temperature was increased, the branching ratio of N\(_2\)O/N\(_2\) became progressively higher on Pd(111), but remained unchanged on Pd(100). Figure 3 shows that as the temperature was increased, the \([\text{NO}]_a/[\text{CO}]_a\) increased up to 10:1 on Pd(111), but stayed below 1:1 on Pd(100). Since the \([\text{NO}]_a\) never exceeds the \([\text{CO}]_a\) on Pd(100), there is no driving

![Figure 7: Apparent activation energies for the CO+NO reaction vs \( P_{\text{NO}}/P_{\text{CO}} \), calculated with the Arrhenius equation.](image-url)
force to produce more N₂O than N₂, even at high temperatures. The N₂O/N₂ branching ratio increases with respect to temperature on Pd(111) due to the direct correlation between [NO]₆/[CO]₆ and temperature (Fig. 3).

V. CONCLUSION

It has been shown that both the higher activity and the higher selectivity (N₂O/N₂) of Pd(111) for the CO+NO reaction are directly related to the higher [NO]₆/[CO]₆ on Pd(111) versus Pd(100). NO TPD data indicate that N₆ (and/or O₆) from dissociated NO inhibits the CO+NO reaction below the N₆ desorption temperature on Pd(100). Apparent activation energy measurements over both surfaces have also shown that as the [NO]₆/[CO]₆ increases, the apparent Eₐ decreases while the activities and N₂O/N₂ selectivities increase. At high temperatures, the higher [NO]₆/[CO]₆ on Pd(111) forces the second, less optimum reaction pathway to dominate because it allows for higher conversion of NO₆. On Pd(100), on the other hand, the [NO]₆/[CO]₆ never exceeds one. This allows reaction (1), with more favorable selectivity, to predominate at all temperatures on this surface.

The measured activities for CO₂ production and the measured selectivities for N₂O vs N₂ production provide firm proof that the CO+NO reaction is structure sensitive over Pd under the conditions studied. The IRAS coadsorption experiments provide support for the higher [NO]₆/[CO]₆ on Pd(111) being a determining factor in the structure sensitivity. TPD data also show structure sensitivity for the stability and surface coverage of N₆ on these two surfaces. These experiments support earlier observations made in this laboratory showing the structure sensitivity of the CO oxidation reaction over Pd(100) and Pd(111). This demonstration of structure sensitivity by correlating surface coverages with high pressure reaction kinetics represents another example of the usefulness and validity of extrapolating results obtained in UHV with “real world” conditions.

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15 Estimated from peak temperatures of TPD spectra of coadsorbed CO and NO.