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# Combined in Situ Infrared and Kinetic Study of the Catalytic CO + NO Reaction on Pd(111) at Pressures up to 240 mbar

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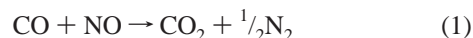
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The CO + NO reaction on Pd(111) has been studied at pressures up to 240 mbar using in situ polarization modulation infrared reflection–absorption spectroscopy (PM-IRAS), which simultaneously provides information on the in situ adsorption behavior as well as the reaction kinetics via gas-phase infrared absorption. Under reaction conditions ( $>500$  K) and at pressure ratios  $P_{\text{CO}}/P_{\text{NO}} \geq 1.5$ , besides CO and NO, isocyanate is adsorbed on the surface as evidenced by isotope experiments. The kinetics of the CO + NO reaction to form CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> was followed by monitoring the evolution of gas-phase CO<sub>2</sub> and N<sub>2</sub>O. Above 550 K, a substantial increase in activity was observed. Kinetic measurements between 590 and 650 K showed an increase in the N<sub>2</sub>O selectivity as a result of temperature-dependent changes of the ratio  $[\text{NO}]_{\text{a}}/[\text{CO}]_{\text{a}}$ . Within this temperature range and on the basis of the CO<sub>2</sub> yields, the apparent activation energy of the reaction was determined to be  $54 \pm 21$  kJ/mol.

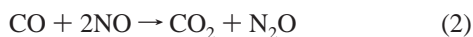
## Introduction

An understanding of the reaction pathways and catalytic characteristics of the CO + NO reaction is of considerable interest because of its commercial importance for three-way catalytic converters (for the simultaneous reduction of NO<sub>x</sub> and the oxidation of CO and unburned hydrocarbons). Therefore, the CO + NO reaction has been studied over various transition- and noble-metal catalysts.<sup>1–14</sup> Recently, Pd-only catalysts have been considered as an alternative to the Pt/Rh (90/10) catalysts that are currently predominantly used.<sup>14–16</sup> Hence, a fundamental understanding of the reaction pathways of the CO + NO reaction on Pd surfaces is of vital importance.

Although the adsorption of CO and NO on low-index planes of palladium has been studied in detail under ultrahigh vacuum conditions,<sup>17</sup> only a few studies have examined the CO + NO reaction over well-defined surfaces at elevated pressures.<sup>2,5,6</sup> Previous studies of the CO + NO reaction on Pd(111) at 2.7–23 mbar have focused on the reaction kinetics and the branching ratio between the desired reaction pathway



and the less ideal pathway



For a 1:1 mixture of CO and NO at 2.7 mbar total pressure, the N<sub>2</sub>O/N<sub>2</sub> ratio increases with increasing temperature.<sup>5</sup> This change in ratio was found to be directly related to the higher  $[\text{NO}]_{\text{a}}/[\text{CO}]_{\text{a}}$  ratio at higher temperatures forcing pathway (2) to dominate.<sup>6</sup> Temperature-programmed desorption (TPD) spectra after exposure to CO and NO at  $10^{-5}$  mbar suggest that stable atomically adsorbed N, which desorbs as N<sub>2</sub> between 500 and 625 K, inhibits the reaction at lower temperatures.<sup>6,14</sup>

According to recent DFT calculations, besides the formation of N<sub>2</sub>, the dissociation of NO appears to inhibit the reaction on Pd(111).<sup>18</sup>

There have been both experimental<sup>19–27</sup> and theoretical<sup>28,29</sup> studies of isocyanate on well-defined transition-metal surfaces. However, metal-bound isocyanate species on well-defined Pd catalysts have not been reported yet. Therefore, their role in the CO + NO reaction is still unexplored. A recent theoretical study addresses the dissociation of NO and the formation of isocyanate in the CO + NO reaction on Pd(111).<sup>28</sup> The activation energy of the  $\text{N} + \text{CO} \rightarrow \text{NCO}$  reaction, assuming that N and CO are adsorbed on high-coordination sites, is found to be 2 eV, which is an intermediate value compared to those for the dissociation of NO (1.5 eV) and CO (3.5 eV).

Infrared transmission studies of the CO + NO reaction on Pd supported on Al<sub>2</sub>O<sub>3</sub><sup>30,31</sup> and aluminosilicates<sup>32</sup> have shown the formation of isocyanate (–NCO) bands around 2240 and 2265 cm<sup>–1</sup>, respectively, which have been attributed to isocyanate bound to the support. It is assumed that isocyanate is first formed on the metal and then subsequently spills over to the substrate. According to the latter study, on sodium-doped Pd/SiO<sub>2</sub> at 573 K, the CO + NO reaction leads to the formation of a band at 2190 cm<sup>–1</sup>, which, without any further confirmation by isotope substitution experiments, has been assigned to metal-bound isocyanate.

The CO + NO reaction has been studied previously over Pd/Al<sub>2</sub>O<sub>3</sub><sup>30,31</sup> and Rh/SiO<sub>2</sub><sup>33–35</sup> catalysts with infrared transmission spectroscopy. Despite these efforts, a detailed understanding of the adsorption behavior during the CO + NO reaction under catalytic conditions has not been obtained yet because of the lack of appropriate in situ techniques. Under high-pressure conditions, the detection of infrared absorption signals of adsorbed species is normally obscured by strong gas-phase absorptions. To circumvent this problem, polarization modulation infrared reflection–absorption spectroscopy (PM-IRAS), an adaption of the well-known IRAS technique, is used. Its surface sensitivity relies on the fact that s- and p-polarized

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infrared light while showing a strong polarization disparity at the metal surface exhibits the same sensitivity for gas-phase absorption. By demodulation, a differential reflectivity spectrum is obtained that is virtually free from gas-phase contributions.

Since CO is in excess of NO in the untreated exhaust gas, our studies have focused on pressure ratios of  $P_{\text{CO}}/P_{\text{NO}} \geq 1$ . In a previous communication, we reported on the formation and stability of isocyanate in the catalytic reaction of CO + NO on Pd(111) at 240 mbar total pressure and a pressure ratio of  $P_{\text{CO}}/P_{\text{NO}} = 1.5$ .<sup>36</sup> Once the isocyanate was produced at temperatures between 500 and 625 K, it was stable within the whole temperature range studied (300–625 K) as well as after reducing the pressure to  $1 \times 10^{-7}$  mbar at room temperature. However, at 600 K, the detection of the isocyanate band on Pd(111) required a total pressure of CO and NO of ca.  $10^{-1}$  mbar, which illustrates the importance of in situ infrared experiments under high-pressure conditions. In the present paper, we address the catalytic CO + NO reaction in more detail by using infrared spectroscopy to examine both the in situ adsorption and the reactivity behavior of the CO + NO reaction on a Pd(111) model catalyst under high-pressure conditions simultaneously.

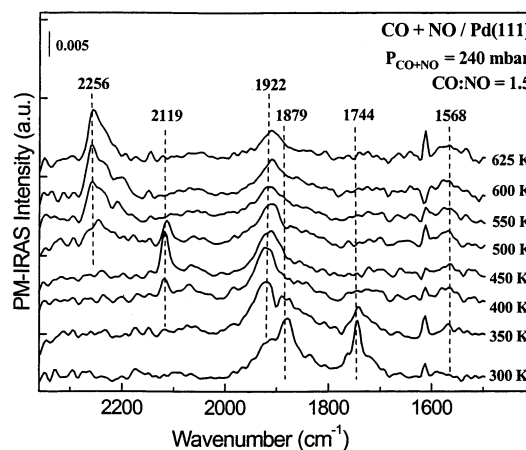
## Experimental Section

The experiments were performed in a combined ultrahigh vacuum (UHV)–microreactor system. The microreactor (total volume: 300 mL) is equipped with  $\text{CaF}_2$  windows and is separated from the UHV chamber via a differentially pumped sliding seal that enables the transfer of the sample from the main chamber to the high-pressure section. The high-pressure reactor is coupled to a Fourier transform infrared spectrometer that allows gas-phase infrared as well as infrared reflection–absorption studies to be performed. The main chamber (base pressure  $< 5 \times 10^{-10}$  mbar) is equipped with surface characterization techniques such as Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and temperature-programmed desorption (TPD). The Pd(111) crystal was cleaned by repeated cycles of oxidation at 650 K and subsequent annealing to 1200 K until its surface was found to be free of carbon, oxygen, and sulfur contamination as measured by AES.<sup>37</sup>

The gases used in the experiments were CO,  $\text{O}_2$ ,  $\text{CO}_2$ , and  $\text{N}_2\text{O}$ , which were of 99.99% purity or better, and NO (C. P. grade). For the isotope experiments,  $^{13}\text{CO}$  (99%) and  $^{15}\text{NO}$  (99%) were used. CO and NO were further purified by using a *n*-pentane/liquid nitrogen slurry that was maintained at 143 K. Prior to high-pressure experiments, CO and NO were premixed for at least 10 h. To avoid any photoinduced  $\text{NO}_2$  formation, both the premixing/cleaning procedures and the experiments were conducted with the exclusion of visible light.

The PM-IRA spectra were obtained with a Fourier transform (FT) IR spectrometer. An extensive description of the experimental setup is given elsewhere.<sup>38</sup> Briefly, the setup consisted of an infrared spectrometer (Bruker Equinox 55), a photoelastic modulator (PEM, Hinds instruments) to create a fast modulation of the polarization state of the incident light (ideally between *s* and *p* states), and a demodulator/multiplexer (GWC instruments, Bruker) to compute a differential reflectivity spectrum from the sum (*p* + *s*) and difference (*p* – *s*) signals collected by the mercury–cadmium–telluride (MCT) detector. For the experiments described below, the PEM controller was set to 1700  $\text{cm}^{-1}$ . The PM-IRA spectra were obtained by sampling for 4.5 min. The spectral resolution was 8  $\text{cm}^{-1}$ .

The CO + NO reaction to form  $\text{CO}_2$ ,  $\text{N}_2$ , and  $\text{N}_2\text{O}$  was performed in a batch mode and followed with infrared spectroscopy by monitoring both the adsorption behavior on the Pd



**Figure 1.** In situ PM-IRA spectra of Pd(111) in the presence of CO + NO (240 mbar,  $P_{\text{CO}}/P_{\text{NO}} = 1.5$ ) as a function of catalyst temperature. During the initial dosage of the mixture, the temperature was kept at 300 K. At temperatures  $\geq 500$  K, an isocyanate-related band at 2256  $\text{cm}^{-1}$  is observed.

surface (via PM-IRAS) and the evolution of the gas-phase  $\text{CO}_2$  and  $\text{N}_2\text{O}$ . The gas-phase production of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  was calculated by converting infrared intensities into pressures by using a set of calibration curves. Turnover frequencies (TOF) were obtained by normalizing the gas-phase production per second to the total number of surface sites.

## Results and Discussion

**A. In Situ Infrared Spectroscopy and Isocyanate Formation.** Figure 1 depicts a series of PM-IRA spectra as a function of catalyst temperature that were obtained in the presence of a 3:2 mixture of CO and NO at a total pressure of 240 mbar. Before starting the experiments, the premixed gases were introduced into the high-pressure cell until an equilibrium pressure of 240 mbar was established while keeping the sample temperature at 300 K. Under non-reaction conditions ( $< 500$  K), the coadsorption of CO and NO leads to the formation of infrared absorption bands at 1568, 1744, 1879, 1922, and 2119  $\text{cm}^{-1}$ . The sharp peak at 1615  $\text{cm}^{-1}$  is due to a strong water-related feature of the high-pressure background.<sup>39</sup> The broad band around 1568  $\text{cm}^{-1}$  is assigned to NO adsorption on 3-fold hollow sites of Pd(111). The 1744  $\text{cm}^{-1}$  band, which is observed below 450 K, is attributed to nitric oxide occupying atop sites. These assignments are based on IRAS/LEED studies and DFT calculations of NO on Pd(111).<sup>40–42</sup> In contrast to the experimental results, in a recent theoretical study on the coadsorption of CO and NO on Pd(111), no NO adsorption on atop sites was found.<sup>43</sup>

Similarly, by comparison with the results of infrared and theoretical studies of CO on Pd(111),<sup>44,45</sup> the bands at 1879 and 2119  $\text{cm}^{-1}$  can be attributed to CO bound to 3-fold hollow and atop sites, respectively.<sup>46</sup> The long-standing assignment of the 1922- $\text{cm}^{-1}$  band to CO on bridge sites has been questioned by several studies that favor 3-fold hollow sites,<sup>45,47,48</sup> but in accordance with recent STM studies, it can be assigned to CO occupying both bridge and 3-fold hollow sites.<sup>49</sup>

When the catalyst temperature was raised, the NO-related band at 1744  $\text{cm}^{-1}$  decreased in intensity and finally disappeared at ca. 450 K. These changes were accompanied by a distinct intensity transfer between the CO-related bands at 1879 and 1922  $\text{cm}^{-1}$  and an increase in the 2119- $\text{cm}^{-1}$  band. Above 450 K, the band around 1900  $\text{cm}^{-1}$  loses intensity, and the band

**TABLE 1: Comparison of the Isocyanate Group Frequencies and Isotope Frequency Shifts (in  $\text{cm}^{-1}$ ) on Pd(111) and Cu(100)**

|                      | $^{14}\text{N}^{12}\text{CO}$ | $^{14}\text{N}^{13}\text{CO}$ | $^{15}\text{N}^{12}\text{CO}$ | $^{13}\text{CO}-^{12}\text{CO}$ | $^{15}\text{NO}-^{14}\text{NO}$ |
|----------------------|-------------------------------|-------------------------------|-------------------------------|---------------------------------|---------------------------------|
| Cu(100) <sup>a</sup> | 2198                          | 2140                          | 2192                          | -58                             | -6                              |
| Pd(111) <sup>b</sup> | 2243                          | 2178                          | 2230                          | -65                             | -13                             |

<sup>a</sup> Celio et al.<sup>20</sup> <sup>b</sup> Hess et al. (current work). For the CO + NO and CO +  $^{15}\text{NO}$  mixtures,  $P_{\text{total}} = 0.67$  mbar ( $\text{CO}/^{14,15}\text{NO} = 1.5$ ), and for the  $^{13}\text{CO}$  + NO mixture,  $P_{\text{total}} = 1.06$  mbar ( $^{13}\text{CO}/\text{NO} = 1.3$ ). Mixtures were dosed at 600 K.

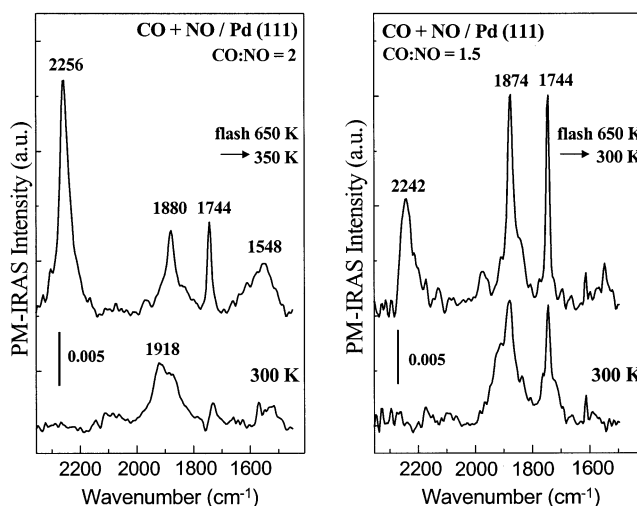
at  $1568\text{ cm}^{-1}$  gains intensity with increasing temperature, which results in an overall increase in the ratio  $[\text{NO}]_{\text{a}}/[\text{CO}]_{\text{a}}$ .

Interestingly, at 500 K, a new band around  $2256\text{ cm}^{-1}$  that can be assigned to neither adsorbed CO nor NO was observed. In addition, bands due to the adsorption of reaction products  $\text{CO}_2$  and  $\text{N}_2\text{O}$  and/or the possible interference of their gas-phase signals (as a result of insufficient subtraction of their strong gas-phase signals) can be ruled out because pressure and temperature-dependent experiments (0–50 mbar, 300–650 K) with pure  $\text{CO}_2$  and  $\text{N}_2\text{O}$  gave no PM-IRA bands within the frequency range studied ( $1500\text{--}2300\text{ cm}^{-1}$ ). Therefore, the feature around  $2256\text{ cm}^{-1}$  is assigned to isocyanate ( $-\text{NCO}$ ), as described in more detail below. When the temperature of the Pd catalyst was raised to 600 K, the intensity of the isocyanate species at  $2256\text{ cm}^{-1}$  increased. Raising the temperature to 625 K led to no further increase in isocyanate intensity.

Previous infrared studies of the CO + NO reaction on a supported palladium catalyst (1.75 wt % Pd/ $\text{Al}_2\text{O}_3$ ) have shown the formation of a broad band at ca.  $2240\text{ cm}^{-1}$ , which has been attributed to isocyanate bound to the alumina support material.<sup>31</sup> To identify the nature of the band observed in the present study on Pd(111), isotope experiments were performed at lower pressures (0.67–1.1 mbar). In Table 1, the results of these experiments are summarized and compared to those of previous isotope experiments on Cu(100).<sup>20</sup> With respect to the isotope shifts, there is good agreement. Similarly, our  $^{13}\text{CO}-^{12}\text{CO}$  frequency shift of  $-65\text{ cm}^{-1}$  compares very well with the  $-60.5\text{ cm}^{-1}$  shift reported for isocyanate adsorbed on Ru(001).<sup>21</sup>

Strictly speaking, the results of our isotope experiments indicate only the presence of C and N. However, because of its high activation barrier (3.5 eV), the dissociation of CO can be ruled out as source of C.<sup>28</sup> In addition, PM-IRAS studies on CO/Pd(111) at  $P_{\text{CO}} = 450$  mbar gave no indication of CO dissociation in the presence of a high-pressure environment.<sup>38</sup> Possible carbon contaminations on the surface cannot act as a C source because of the isotope shift observed for the  $^{13}\text{CO}/\text{NO}$  mixture. This leaves the intact CO molecule as the only possible source of C and rules out the formation of cyano ( $-\text{CN}$ ), isocyano ( $-\text{NC}$ ), fulminato ( $-\text{CNO}$ ), or isofulminato ( $-\text{ONC}$ ) groups. Besides the isocyanate group ( $-\text{NCO}$ ), only the cyanato group ( $-\text{OCN}$ ) can account for the above-mentioned experiments. However, a large number of isocyanate-containing Pd complexes are known, in contrast to the number of Pd complexes containing cyanato groups.<sup>50</sup> In addition, according to a theoretical study, on Ni(100) isocyanate was found to be more stable than cyanate by 16 kcal/mol.<sup>29</sup> Therefore, the infrared feature observed around  $2256\text{ cm}^{-1}$  can be attributed to the asymmetric stretching mode of an isocyanate group. However, because of the asymmetric shape of the band, a contribution from other surface species cannot be excluded.

In a different set of experiments, the stability of the isocyanate species after its formation at elevated pressures was addressed. Figure 2 shows PM-IRA spectra obtained in the presence of a



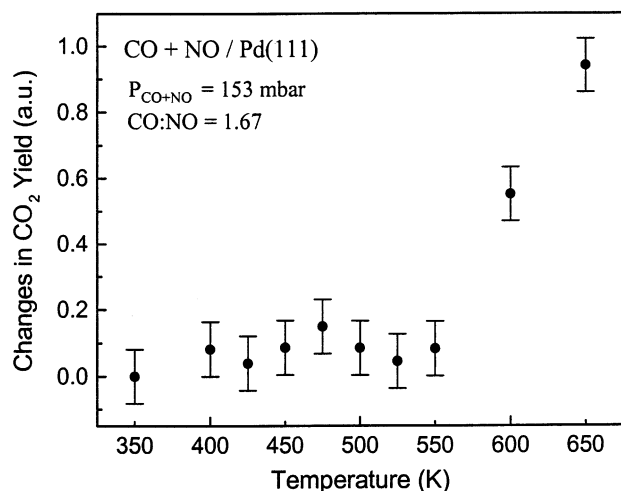
**Figure 2.** PM-IRA spectra of Pd(111) in the presence of a CO + NO mixture at pressure ratios of  $P_{\text{CO}}/P_{\text{NO}} = 1.5$  (right) and 2 (left) and total pressures of 240 and 180 mbar, respectively. The upper spectra were obtained after heating the catalyst to 650 K.

CO + NO mixture at pressure ratios of  $P_{\text{CO}}/P_{\text{NO}} = 2$  (left) and 1.5 (right) and total pressures of 180 and 240 mbar, respectively. After introducing the gas mixture into the high-pressure cell and its equilibration with the catalyst at 300 K, the spectra shown on the bottom of Figure 2 were obtained. They are characterized by infrared bands around 1550, 1750, and  $1880\text{ cm}^{-1}$ , which can be assigned to 3-fold hollow NO, atop NO, and 3-fold hollow CO, respectively (see above). The preferential atop adsorption of NO and 3-fold hollow adsorption of CO in a CO/NO overlayer have been observed before at  $10^{-6}$  mbar total pressure and have been explained by the higher stability of atop NO compared to that of atop CO in the pure adsorbate overlayers.<sup>51</sup> As shown in the bottom spectra of Figure 2, a higher CO/NO pressure ratio increases the relative CO coverage in the mixed CO/NO overlayer.

After the samples were heated to 650 K and cooled back to room temperature in the presence of the CO + NO mixture, the spectra depicted on the top of Figure 2 were recorded. As outlined above, under reaction conditions, isocyanate is formed. During the whole cooling process and after cooling the catalyst to room temperature, the isocyanate species was still present. As shown in Figure 2, an increase in the CO/NO pressure ratio strongly favored the formation of isocyanate. Similarly, in previous experiments on a supported Rh catalyst, the presence of excess CO led to a strong increase in isocyanate formation while showing only a small isocyanate band for a stoichiometric CO/NO mixture.<sup>35</sup> The preferred formation of surface isocyanate for  $P_{\text{CO}}/P_{\text{NO}} = 2$  leads to a decrease in the overall CO + NO coverage after annealing compared to that for  $P_{\text{CO}}/P_{\text{NO}} = 1.5$ , as can be rationalized on the basis of intensity changes in the bands at 1548, 1744, and  $1880\text{ cm}^{-1}$ . As has been shown in a coverage-dependent infrared study on the coadsorption of CO and NO on Pd(111),<sup>5</sup> an increase in coverage (when starting at a CO + NO coverage comparable to the one at which the spectrum at the top left of Figure 2 was taken) leads to the disappearance of the  $1548\text{-cm}^{-1}$  band but an intensity gain in the 1744- and  $1880\text{-cm}^{-1}$  bands.

It can be seen in Figure 2 that the isocyanate bands peak at  $2242\text{ cm}^{-1}$  for  $P_{\text{CO}}/P_{\text{NO}} = 1.5$  and at  $2256\text{ cm}^{-1}$  for  $P_{\text{CO}}/P_{\text{NO}} = 2$ . As already indicated by the change in peak area, the blue shift of the asymmetric stretch frequency is due to an increase in isocyanate coverage, in agreement with previous studies on





**Figure 3.** Changes in the CO<sub>2</sub> yield of the CO + NO reaction on Pd(111) as a function of catalyst temperature at 153 mbar total pressure ( $P_{\text{CO}}/P_{\text{NO}} = 1.67$ ).

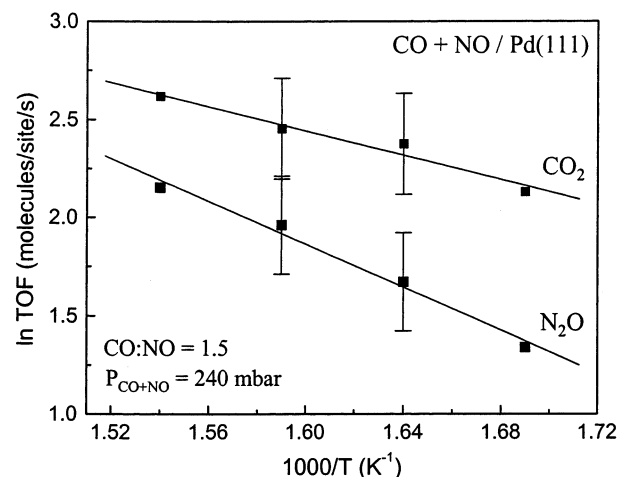
Cu(100).<sup>20</sup> Similarly, the isocyanate frequency shows a 14-cm<sup>-1</sup> red shift for  $P_{\text{CO}}/P_{\text{NO}} = 1.5$  when cooling from 600 K (see Figure 1) to room temperature (see Figure 2), indicating a decrease in isocyanate coverage when leaving the reaction regime.

It is apparent from Figure 2 that annealing of the sample leads to a significant reduction in the line width of the infrared bands around 1744 and 1880 cm<sup>-1</sup>. Obviously, by cooling the sample in the presence of the gas mixture, a higher degree of surface order can be achieved than with room-temperature adsorption. Similar behavior has been observed for the adsorption of CO on Pd(111).<sup>52</sup> However, a quantitative treatment of these order-disorder phenomena on the basis of infrared spectra is difficult because the CO + NO reaction leads to residuals on the surface (e.g., N<sub>a</sub> and O<sub>a</sub>) that may effect the line width of the observed bands.

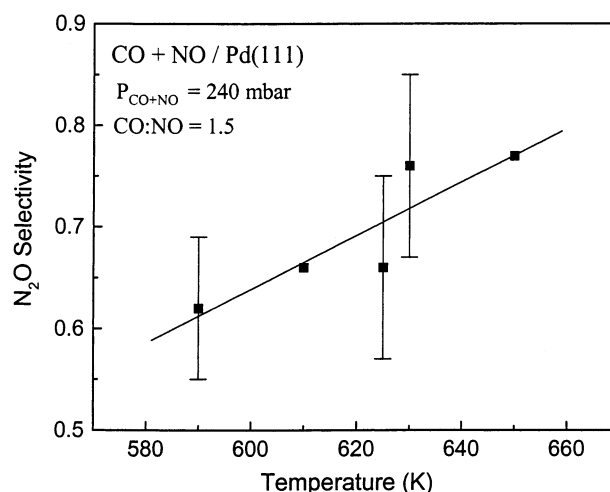
**B. Kinetics of the CO + NO Reaction.** Figure 3 shows the changes in the CO<sub>2</sub> yield of the CO + NO reaction as a function of catalyst temperature at a total pressure of 153 mbar ( $P_{\text{CO}}/P_{\text{NO}} = 1.67$ ). The CO<sub>2</sub> yield was obtained by measuring the increase in the CO<sub>2</sub> gas-phase absorption after a 4.5-min run and subsequently increasing the temperature to the next value.<sup>53</sup> Whereas below 550 K no significant changes in the CO<sub>2</sub> yield were observed, higher temperatures led to a strong increase in the CO<sub>2</sub> yield. This behavior shows that the CO + NO reaction on Pd(111) is associated with an energy barrier that is effectively overcome above 550 K.

Figure 4 depicts the turnover frequencies (TOFs) for the produced gas-phase CO<sub>2</sub> and N<sub>2</sub>O within the temperature range of 590–650 K in an Arrhenius plot. In these experiments, the pressure ratio of CO and NO was  $P_{\text{CO}}/P_{\text{NO}} = 1.5$ , and the total pressure was 240 mbar. Both the CO<sub>2</sub> and N<sub>2</sub>O values show an increase with increasing temperature. Assuming that no coking of the catalyst occurred, the total CO conversion is accurately measured by the concentration of CO<sub>2</sub> that is formed via reactions (1) and (2). In contrast, the total NO conversion equals the sum of the N<sub>2</sub> and N<sub>2</sub>O concentrations produced. Although the N<sub>2</sub> production cannot be measured via IR spectroscopy, the concentration of N<sub>2</sub> produced can be determined from reactions (1) and (2):

$$[\text{N}_2] = \frac{1}{2}([\text{CO}_2] - [\text{N}_2\text{O}]) \quad (3)$$



**Figure 4.** Arrhenius plot for the production of CO<sub>2</sub> and N<sub>2</sub>O in the CO + NO reaction on Pd(111) at 240 mbar total pressure ( $P_{\text{CO}}/P_{\text{NO}} = 1.5$ ).



**Figure 5.** N<sub>2</sub>O selectivities, N<sub>2</sub>O/(N<sub>2</sub> + N<sub>2</sub>O), for the CO + NO reaction on Pd(111) at 240 mbar total pressure ( $P_{\text{CO}}/P_{\text{NO}} = 1.5$ ).

Using reaction (3), the selectivity for N<sub>2</sub>O, N<sub>2</sub>O/(N<sub>2</sub> + N<sub>2</sub>O), can be calculated. N<sub>2</sub>O selectivities for the results presented above are given in Figure 5. They range from 0.62 at 590 K to 0.77 at 650 K (i.e., with increasing catalyst temperature, the formation of N<sub>2</sub>O is favored).

The temperature-dependent gas-phase yields allow for the determination of the activation energy of the CO + NO reaction in the presence of 240 mbar total pressure. On the basis of the CO<sub>2</sub> yields, an apparent activation energy of  $54 \pm 21$  kJ/mol is obtained by using an Arrhenius plot. This value is slightly lower than the corresponding low-pressure value of 66 kJ/mol.<sup>5</sup>

**C. Comparison of Infrared and Kinetic Results.** The catalytic activity of Pd(111) to form CO<sub>2</sub>, N<sub>2</sub>O, and N<sub>2</sub> in the presence of a CO/NO mixture at elevated pressure (153 mbar) increases significantly above 500 K, as shown in Figure 3. This behavior is in agreement with previous results obtained at lower pressures and has been attributed to the presence of energy barriers for the NO dissociation and N<sub>2</sub> formation that are inhibiting for the rate of the CO + NO reaction.<sup>5,6,18</sup> Besides the activities for the production of CO<sub>2</sub> and N<sub>2</sub>O, the N<sub>2</sub>O selectivity and the activation enthalpy for the CO + NO reaction are in good agreement with the results obtained at 2.7 mbar.<sup>5</sup> Within the scope of the present study, the differences in the IR spectra described above, in particular, the presence of isocyanate,

did not lead to measurable changes in the reactivity behavior as compared to that of the low-pressure work. If, in addition, the stability of the isocyanate species is taken into account, it is likely that under the experimental conditions studied here the isocyanate species plays the role of a spectator rather than an intermediate in the CO + NO reaction.

Changes in  $[\text{NO}]_a/[\text{CO}]_a$ , as determined from infrared measurements, can provide insight into the origin of the measured  $\text{N}_2\text{O}$  selectivities in the CO + NO reaction on Pd(111).<sup>5</sup> As outlined above, above 500 K, both the ratio  $[\text{NO}]_a/[\text{CO}]_a$  and the  $\text{N}_2\text{O}$  selectivity increase with increasing temperature. It therefore appears as if the higher  $[\text{NO}]_a/[\text{CO}]_a$  forces the second, less desirable reaction pathway (2) to dominate because it consumes more NO than pathway (1).

The observation of isocyanate provides valuable information on the mechanism of the CO + NO reaction on Pd(111) because its formation requires the dissociation of NO, which is considered to be a crucial step in the CO + NO reaction. Therefore, the onset of isocyanate formation may serve as a sensitive indicator for the dissociation of NO on Pd(111). The fact that the formation of isocyanate sets in at 500 K (Figure 1) but the formation of the reaction products sets in at temperatures above 550 K (Figure 3) indicates that below 550 K the CO + NO reaction may be inhibited by reaction steps other than the dissociation of NO such as, for example, the removal of stable  $\text{N}_a$  by the formation of  $\text{N}_2$ .

## Conclusions

In the present study, infrared spectroscopy has been used to examine both the in situ adsorption behavior and the kinetics of the CO + NO reaction on Pd(111) under high-pressure conditions. It has been shown that, under reaction conditions, metal-bound isocyanate is formed. Once isocyanate is formed it is stable within 300–625 K (i.e., even outside the reaction regime of the CO + NO reaction). The observation of isocyanate provides valuable information on the mechanism of the CO + NO reaction because its formation implies the dissociation of NO, which is a crucial step in the CO + NO reaction on Pd(111).

It has been shown by gas-phase absorption infrared spectroscopy that the measured activities for  $\text{CO}_2$  and  $\text{N}_2\text{O}$  production as well as the measured  $\text{N}_2\text{O}$  selectivities are in good agreement with previous results obtained at lower pressures. At high temperatures, the higher  $[\text{NO}]_a/[\text{CO}]_a$  forces the less desirable reaction pathway to dominate because it allows for a higher conversion of adsorbed NO. For the temperature range 590–650 K, the apparent activation energy of the CO + NO reaction was determined to be  $54 \pm 21$  kJ/mol.

Considering the stability of the isocyanate species and the similar reactivity behavior of the CO + NO reaction in high-pressure and low-pressure experiments that gave no indication of isocyanate formation, it is most probable that under the conditions studied here isocyanate plays the role of a spectator rather than an intermediate in the CO + NO reaction. However, the fact that the formation of isocyanate can be observed only at elevated pressure shows that in situ studies under more “realistic” conditions are necessary to obtain a detailed understanding of surface reactions.

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