Isocyanate Formation in the Catalytic Reaction of CO + NO on Pd(111): An in Situ Infrared Spectroscopic Study at Elevated Pressures

Emrah Ozensoy, Christian Hess, and D. Wayne Goodman*

Department of Chemistry, Texas A&M University, P.O. Box 30012, College Station, Texas 77842-3012

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The catalytic conversion of environmentally hazardous pollutants in automobile exhausts is one of the most thoroughly studied problems in heterogeneous catalysis. Three-way catalysts (TWC) are used to remove the major pollutants in the exhaust gases by the simultaneous reduction of NO_x and the oxidation of CO and unburned hydrocarbons. Recently, Pd-based catalysts have been considered as an alternative to the more commonly used Pt/Rh-based catalysts.[1,2] In this study vibrational spectroscopy is used to examine the in situ adsorption of CO + NO to form CO_2, N_2O and N_2 on a Pd(111) model catalyst under high-pressure conditions. We employ polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS),[3-5] an adaption of the well-known IRAS technique. The surface sensitivity of PM-IRAS relies on the fact that IR absorption by an adsorbed species on a metal surface shows a strong dependence on the polarization of the incoming IR beam, while gas-phase species are isotropic with respect to the polarization.

Figure 1 shows PM-IRA spectra of Pd(111) in the presence of a 240 mbar CO + NO mixture within the temperature range 300–600 K (CO:NO = 3:2). The spectra were obtained by increasing the CO + NO gas mixture pressure at $T_{surface}$ = 300 K until an equilibrium pressure of 240 mbar was established. The data were acquired in the presence of 240 mbar of ambient pressure at the given temperatures. The spectrum at 350 K shows a feature at 1922 cm^{-1}, which corresponds to CO residing on either two-fold or three-fold Pd sites.[6-10] The feature at 1876 cm^{-1} can be assigned to CO located on the three-fold sites[7, 8-10] while the peak at 1745 cm^{-1} is assigned to NO bound to atop sites.[11] At 350 K, atop sites are predominantly occupied by NO whereas three-fold sites are occupied by CO and possibly NO (considering the broad band at approximately 1550 cm^{-1}). Interestingly, at 600 K and under reaction conditions, the spectrum is dominated by a new band at 2255 cm^{-1} besides the CO-related feature at 1908 cm^{-1}. The feature at 2255 cm^{-1} is assigned to the asymmetric stretching mode of an isocyanate (−NCO) species.[12-20] Once produced at high temperatures (500–625 K), this species is stable within the 300–625 K temperature range as well as after reducing the chamber pressure to 1×10^{-7} mbar at room temperature. In previous infrared studies on Pd/Al_2O_3 [16,17] a broad band near 2242 cm^{-1} has been observed and assigned to a substrate-bound isocyanate species. According to these previous studies, the formation of isocyanate takes place on metal sites followed by spillover to the substrate. Although a metal-bound isocyanate species was not reported for the Pd/Al_2O_3 system,[16] isocyanate formation in the CO + NO reaction on Pd(111) was postulated in a recent theoretical study.[20]

To explore the conditions under which the metal-bound isocyanate species is formed on Pd(111), experiments with different total pressures were conducted (see Figure 2). At 10^{-4} mbar a feature

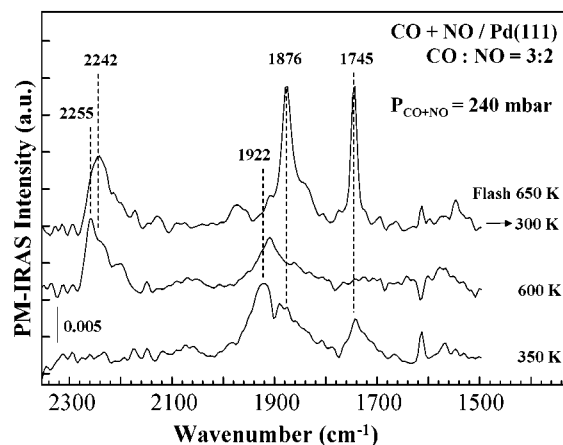* To whom correspondence should be addressed. E-mail: goodman@mail.chem.tamu.edu.

Figure 1. In situ PM-IRA spectra of Pd(111) in the presence of a CO + NO mixture at 240 mbar (CO:NO = 3:2). The initial dosage was at $T_{surface}$ = 300 K. At 600 K, i.e., under reaction conditions, the formation of an isocyanate-related feature at 2255 cm^{-1} is visible.
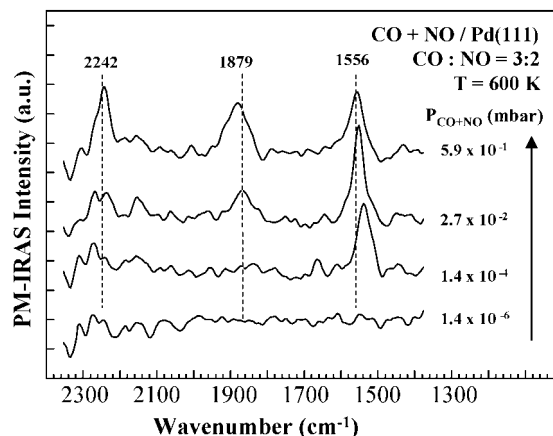

Figure 2. In situ PM-IRA spectra of Pd(111) at 600 K in the presence of a CO + NO gas mixture (CO:NO = 3:2) within 1.4×10^{-6}- 5.9×10^{-1} mbar. The formation of isocyanate was observed only at elevated pressures.

around 1538 cm^{-1} is observed and assigned to NO bound to three-fold sites on Pd(111).[11,21,22] After increasing the CO + NO pressure to approximately 10^{-2} mbar an additional feature at 1879 cm^{-1} is observed and assigned to CO adsorbed on three-fold Pd sites.[6] To observe the formation of the isocyanate feature (at 2242 cm^{-1}), a further increase in pressure to 0.6 mbar is required. Even upon exposure of the Pd(111) surface to 10^{-6}, 10^{-4}, and 10^{-2} mbar of CO + NO at 600 K for about 25 min, no NCO-related features were observed. Therefore, under the experimental conditions employed (i.e., 10^{-6}–10^{-1} mbar, 600 K, CO:NO = 3:2) the detection of the isocyanate features requires a pressure threshold of ca. 10^{-1} mbar.

Table 1. Comparison of Isocyanate Group Frequencies and Isotope Frequency Shifts (in cm^{-1}) on Pd(111) and Pt/Al$_2$O$_3$ in the CO + NO Reaction

	Pt/Al$_2$O$_3$ [a]	Pd(111)[b]
CO + NO	2261	2243
^{13}CO + NO	2199	2178
CO + ^{15}NO	2249	2230
^{13}CO − ^{12}CO	−62	−65
^{15}NO − ^{14}NO	−12	−13

[a] Unland et al.,[14] CO + NO mixtures contained 13.3 mbar CO (or ^{13}CO), 6.7 mbar NO (or ^{15}NO) and 113 mbar N$_2$, dosed at 673 K. [b] Ozensoy and Hess et al. (current work), for the CO + NO and CO + ^{15}NO mixtures P$_{total}$ = 0.67 mbar (CO:^{14,15}NO = 1.5) and for the ^{13}CO + NO mixture P$_{total}$ = 1.06 mbar (^{13}CO:NO = 1.3). Mixtures were dosed at 600 K.

To verify the nature of the observed feature at 2240−2257 cm^{-1}, isotope experiments were performed. The results of these experiments are summarized in Table 1 and compared with previous results obtained for isocyanate species on Pt/Al$_2$O$_3$.[14] There is good agreement between these two studies concerning the isotopic shifts. Our current isotopic studies on Pd(111) indicate that the surface feature corresponding to the vibrational band at 2240−2257 cm^{-1} contains both C and N. However, considering previous experimental[6−10] and theoretical[23] studies concerning CO adsorption on Pd(111), CO dissociation leading to atomic C can be ruled out due to its high activation energy (4.4 eV).[23] Therefore, intact CO molecules adsorbed on Pd(111) can be the only source of the carbon for the observed species, which further supports the assignment mentioned above.

Our current infrared results show that the formation of the −NCO species on Pd(111) begins at approximately 500 K (at 240 mbar of CO + NO) and markedly increases when the temperature is increased to 600 K. Within this temperature regime, a dramatic increase in the reaction rate was observed over Pd(111) at lower pressures.[9] A strong increase in the reaction rate with increasing temperature within 500−600 K was also observed under high-pressure conditions by quantitatively following the formation of CO$_2$(g) and N$_2$O(g) by infrared spectroscopy. The corresponding values for the selectivity and turnover frequency (TOF) are in agreement with previous studies for Pd(111) at 2.7 mbar.[9] Details regarding the kinetics and in situ adsorption behavior of Pd(111) under high-pressure reaction conditions will be presented in a forthcoming publication.

The detection of −NCO at temperatures >500 K and its stability within a wide temperature range may provide important information concerning the CO + NO reaction on Pd(111). For example, the formation of the −NCO species on the surface implies NO dissociation on Pd(111). As shown in Figure 3, NO dissociation can be followed by the reaction of atomic nitrogen with CO yielding a metal-bound isocyanate species on Pd(111). Because both the formation of isocyanate[20] and the CO + NO reaction[8−10] are believed to depend crucially on the dissociation of NO, the detection of the isocyanate species may, due to its high infrared cross section, serve as a sensitive indicator for the onset of the CO + NO reaction. On the other hand, due to its stability, metal-bound isocyanate most probably acts as a spectator in the CO + NO reaction on Pd(111).

In summary, using in situ PM-IRAS the CO + NO reaction on a Pd(111) model catalyst was studied at elevated pressures (up to
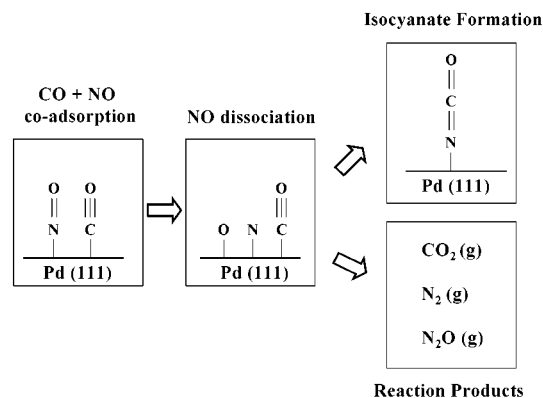

Figure 3. Reaction pathways of the CO + NO reaction on Pd(111).

240 mbar). The results presented in this work provide direct evidence for the formation of an isocyanate (−NCO) species on Pd-sites under reaction conditions (500−600 K). In addition, below 0.01 mbar of CO and NO, no isocyanate features were detected which illustrates the importance of carrying out in situ spectroscopic experiments under high-pressure conditions with a surface specific technique such as PM-IRAS.

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