

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

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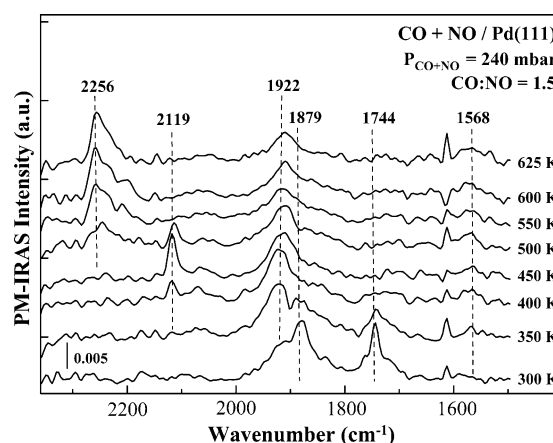
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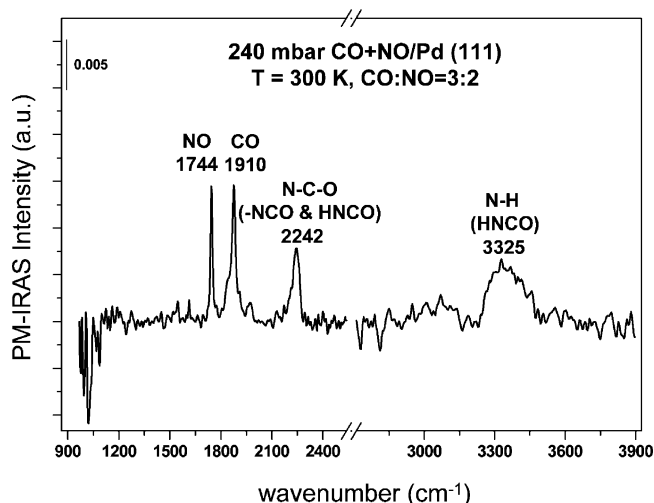
Due its importance for the CO + NO reaction, the adsorption of isocyanate has been studied extensively in the past, both on model catalysts under UHV conditions and on high-surface area catalysts.<sup>1–14</sup> However, the first experiments on single crystal surfaces at elevated pressures (up to 240 mbar) have been performed only recently.<sup>15,16</sup> In these experiments, a Pd(111) model catalyst has been exposed to a CO + NO mixture at 240 mbar total pressure at 300 K and subsequently heated to 650 K (see Figure 1). On the basis of the results of isotope experiments, the occurrence of a broad IR band around 2250 cm<sup>-1</sup> at 500–625 K had been assigned to isocyanate (–NCO) formation during CO + NO reaction. In previous (UHV) experiments on single crystal surfaces, frequencies of the asymmetric stretching mode of adsorbed isocyanate of typically 2170–2190 cm<sup>-1</sup> have been observed.<sup>17–23</sup> On the other hand, coverage-dependent results of isocyanate adsorption on Cu(100) have shown that dipole–dipole interactions can give rise to blue shifts of the asymmetric stretch of the order of ~50 cm<sup>-1</sup>, leading to a high-coverage limit of the frequency of 2227 cm<sup>-1</sup> on Cu(100).<sup>19</sup> In these experiments, even after annealing to 600 K, a strong isocyanate band was observed. In contrast, on Pt(111), Rh(111), and Ru(001), adsorbed isocyanate decomposes/desorbs at ~370 K.<sup>17,20</sup>

Interestingly, on Pt(100), at higher pressures of ~7 × 10<sup>-7</sup> mbar and in the presence of an excess of CO, isocyanate can be stabilized up to ~450 K.<sup>23</sup> Along those lines, recent results on molecular adsorption of CO on single crystal surfaces, e.g., Pd(111), have shown that a high-pressure environment can stabilize the same coverages (as those observed under UHV conditions) at significantly higher temperatures.<sup>24</sup> Another important factor enhancing the stability of the –NCO species has been reported to be the presence of atomic O.<sup>18</sup> The presence of atomic O also results in an additional blue shift of 22 cm<sup>-1</sup> of the –NCO asymmetric stretching band on Rh(111).<sup>18</sup>

The asymmetric shape of the band at 2256 cm<sup>-1</sup> clearly indicates a contribution from at least two species, as has already been pointed out in reference 16. As shown in Figure 2, the experimental data for the CO + NO reaction over Pd(111) at 240 mbar exhibits an additional band around 3325 cm<sup>-1</sup>, which can be assigned to the N–H stretching mode of adsorbed HNCO. This assignment is supported by recent studies on the molecular adsorption of HNCO on Pt(111),<sup>17</sup> Rh(111),<sup>18</sup> and Cu(100),<sup>19</sup> which have reported N–H stretching bands at 3240, 3373, 3292 cm<sup>-1</sup>, respectively, and NCO asymmetric stretching



**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.



**Figure 2.** In situ PM-IRA spectra of Pd(111) in the presence of CO + NO (240 mbar,  $P_{\text{CO}}/P_{\text{NO}} = 1.5$ ) at 300 K. The spectrum was obtained after dosing the gas mixture, annealing to 600 K, and cooling back to 300 K.

bands at 2270, 2277, and 2260 cm<sup>-1</sup>, respectively. However, the band at ~3325 cm<sup>-1</sup> cannot be attributed to an N–H stretch vibration of NH<sub>3</sub> or NH<sub>2</sub> adsorbed on Pd(111) by comparison with previous vibrational spectroscopic studies.<sup>25–32</sup> These studies indicate that that NH<sub>3</sub> (NH<sub>2</sub>) adsorption on various transition metal surfaces leads to vibrational features at ~1100 (1320), ~1600 (1520), and 3200–3500 cm<sup>-1</sup> that are associated with the symmetric deformation (rocking), asymmetric deformation (scissoring), and N–H stretching modes of molecularly adsorbed NH<sub>3</sub> (NH<sub>2</sub>). Furthermore, in these studies the N–H stretching band (3200–3500 cm<sup>-1</sup>) was accompanied by a symmetric deformation band (~1100 cm<sup>-1</sup> and ~1300 cm<sup>-1</sup>), which had intensity equal to or greater than the N–H stretching band. It is apparent from Figure 2 that a strong absorption around 1100 cm<sup>-1</sup> and 1300 cm<sup>-1</sup> is absent and therefore the presence of significant amounts of adsorbed NH<sub>3</sub> or NH<sub>2</sub> can be excluded. Adsorbed NH has been reported to give rise to only one weak band > 1100 cm<sup>-1</sup>, which appears around 3300 cm<sup>-1</sup><sup>32</sup> and a small contribution from this species cannot be ruled out. In addition, the feature at 3325 cm<sup>-1</sup> in Figure 2 is not associated

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with H<sub>2</sub>O or –OH species, as H<sub>2</sub>O adsorption on Pd (111) leads to strong bands at 3400 cm<sup>−1</sup> (O–H stretch) and 1616 cm<sup>−1</sup> (scissoring) while –OH adsorption results in an O–H stretch at 3400 cm<sup>−1</sup>.<sup>33</sup> Since no IR band at ~1600 cm<sup>−1</sup> is observed in Figure 2 and the observed feature at 3325 cm<sup>−1</sup> has a rather low frequency with respect to an O–H stretching feature on Pd (111), the presence of H<sub>2</sub>O or –OH can also be excluded.

It should be noted that the peak position of the band at 2256 cm<sup>−1</sup> in Figure 1 is in good agreement with the NCO asymmetric stretching band for a molecular HNCO species. On the other hand, in most of the studies mentioned above,<sup>17–19</sup> molecular HNCO species have been found to be significantly less stable than –NCO species and have therefore been used as a precursor for –NCO formation.

Based on the above discussion regarding the coverage dependent frequency shifts for –NCO species and the stabilization effect of atomic O, assigning the main part of the band at 2256 cm<sup>−1</sup> to adsorbed HNCO (with H originating from the bulk of the Pd crystal) and the long-wavelength tail to adsorbed NCO is in good agreement with previous frequency values and the outcome of the isotope experiments.

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