

Formation of Surface CN from the Coupling of C and N Atoms on Pt(111)

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Surface coupling reactions are of broad importance yet are often difficult to replicate under the ultrahigh vacuum (UHV) conditions needed for detailed mechanistic studies of the relevant surface processes. The C–N coupling reaction is the key step in the catalytic synthesis of HCN, an important chemical intermediate in nylon production, from NH_3 and CH_4 over Pt gauze catalysts.¹ Industrially, the synthesis of HCN takes place near atmospheric pressures and at temperatures in the range of 1100–1300 °C. The HCN formation reaction has been the subject of several laboratory-scale model-reactor studies at both atmospheric and reduced pressure.² In an overview of such studies, Schmidt and Hickman³ noted that thermodynamics implies that the highly endothermic reaction of $\text{CH}_4 + \text{NH}_3 \rightarrow \text{HCN} + 3\text{H}_2$ should not occur at all at temperatures below 1000 K. The kinetics of HCN formation was studied in detail by Hasenberg and Schmidt in both the absence^{2b,c} and presence^{2e} of O_2 . Although their kinetic studies provided indirect evidence for the coupling of surface C and N atoms to form CN ,^{2c} which is then hydrogenated to HCN, direct support for this mechanism has been lacking. Alternatively, surface CH_x and NH_y may couple to form a species that then dehydrogenates to HCN.^{2b} Therefore, the identification of the surface species that combine to form C–N bonds is of central importance to establishing the mechanism of the catalytic production of HCN. Here we use temperature-programmed desorption (TPD) to observe HCN desorption and reflection absorption infrared spectroscopy (RAIRS) to observe aminocarbyne, a product of surface CN hydrogenation, following reaction of surface species produced from the decomposition of CH_3I and NH_3 on the Pt(111) surface.

Because neither CH_4 nor NH_3 thermally dissociate on Pt(111) under UHV conditions,^{4,5} other means must be used to generate the surface intermediates that form under the more extreme conditions used in the catalytic synthesis of HCN. The generation of surface intermediates in UHV so that their subsequent surface chemistry can be studied has been a highly successful approach for gaining a basic understanding of reaction mechanisms underlying heterogeneous catalysis.⁶ Surface CH_x ($x = 3, 2, 1, 0$) is most easily generated through adsorption of CH_3I since the weak C–I bond dissociates below 200 K to yield surface CH_3 groups, which then further decompose stepwise to finally give C atoms.⁷ A comparison of the surface chemistry on Pt(111) of CH_3 deposited from the gas phase with CH_3 produced from CH_3I dissociation shows that the I exerts little influence, except for a site-blocking effect at higher coverages.⁸ The preparation of surface NH_y ($y = 2, 1, 0$) species from ammonia can be achieved in several ways. Vajo et al. found ready decomposition under a steady flux at pressures of $(1-2) \times 10^{-6}$ Torr and temperatures of 300–600 K.⁹ An alternative approach is to bombard an ammonia-covered surface with low energy (100 eV) electrons, which we have found can generate both NH_2 and NH species, in agreement with previous studies.¹⁰

The experiments were performed in a UHV system that has been described in detail elsewhere.¹¹ We used a liquid nitrogen-cooled

MCT (HgCdTe) detector with a low wavenumber cutoff near 800 cm^{-1} . In addition to a standard SiC source, a high-temperature homemade graphite source with a working temperature of 2500 K coupled externally to the FTIR has been used to increase the signal-to-noise (S/N) ratio. The methyl iodide was purchased from Alfa Aesar Co. with a quoted purity of 99.5% and was further purified by a procedure described in detail elsewhere.¹² The NH_3 and H_2 were purchased from Matheson Tri-Gas Inc. with quoted purities of 99.9992% and 99.9999%, respectively. The Pt(111) surface was cleaned by a procedure described earlier.¹³

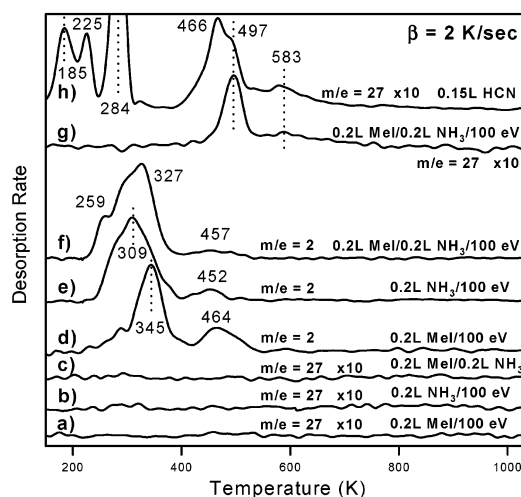


Figure 1. (a)–(g) TPD spectra for $m/e = 27$ (HCN) and 2 (H_2) obtained for a linear heating rate of 2 K s^{-1} for the indicated combinations of NH_3 , CH_3I , and 100 eV electrons (1.5×10^{15} electrons cm^{-2}). (h) TPD spectrum for $m/e = 27$ obtained after a 0.15 L HCN exposure at 85 K.

The fact that the C–N coupling reaction can be induced on Pt(111) under UHV conditions starting from a surface covered with methyl and ammonia fragments is demonstrated by the TPD results in Figure 1. Under the right combination of CH_3I and NH_3 exposures and e^- beam irradiation, HCN ($m/e = 27$) desorption is observed (Figure 1g). In particular, the fact that HCN does not desorb in the absence of e^- beam exposure (Figure 1c) shows that C–N coupling does not occur from a reaction of CH_3 and NH_3 , but rather from their dissociation products. Parts a and b of Figure 1 are control experiments that show that the $m/e = 27$ peak in Figure 1g is not an artifact related to e^- beam exposure. Parts d–f of Figure 1 are the $m/e = 2$ results corresponding to the $m/e = 27$ results in Figure 1a,b,g. Figure 1h shows the $m/e = 27$ result following exposure to 0.15 L of HCN, which agrees with previous results.¹⁴ The highest temperature peaks for HCN desorption in Figure 1h are at 466 K, with a shoulder at 497 K, and at 583 K, with the latter peak part of a high-temperature tail. The presence of the high-temperature tail in Figure 1g,h indicates that it is not specific to the C–N coupling reaction, nor is it due to coadsorbed species that are not present following HCN adsorption on the clean surface.

In a TPD study of HCN on the Pt(111) and stepped Pt(211) surfaces,^{14b} the high-temperature tail was observed to be much more intense for the latter, indicating that it is associated with the steps. Since the CN bond of HCN does not dissociate on Pt(111), the desorption of HCN at 497 K in Figure 1g is consistent with CN bond formation at or below this temperature. The conditions used in Figure 1g were established from a series of TPD experiments following e⁻ beam exposures with different CH₃I:NH₃ coverage ratios in which the maximum *m/e* = 27 signal was found to occur for a ratio of approximately 0.1 ML (0.2 L) of CH₃I: 0.9 ML (0.2 L) of NH₃. Although the existence of the C–N coupling reaction is established by the HCN desorption observed in Figure 1g, this does not establish the CN bond formation temperature.

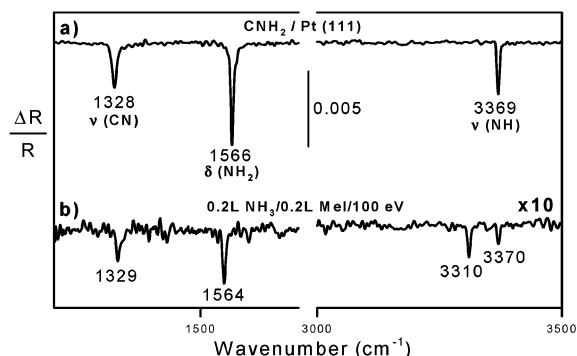


Figure 2. (a) RAIRS spectrum following exposure of the sample to 0.3 L of HCN and 1 L of H₂ at 85 K, followed by annealing to 300 K and cooling to 85 K, where the spectrum was obtained with a SiC (Glowbar) source (1500 K). (b) RAIRS spectrum recorded at 85 K after annealing 0.2 L of NH₃ and 0.2 L of CH₃I exposed to 1.5×10^{15} electrons cm⁻² to 500 K, cooling to 300 K, and exposing to 10 L of H₂. Spectrum (b) was acquired by using a high-temperature graphite source (2500 K).

Our group has demonstrated in numerous studies that surface CN, while not directly detectable with RAIRS, is readily hydrogenated at room temperature to the aminocarbyne species (>CNH₂), which has a strong and characteristic vibrational spectrum.^{13,15} Therefore, we should expect to see the aminocarbyne spectrum if CN bond formation occurs at temperatures below the onset of H₂ desorption at around 350 K. On the other hand, if the formation temperature is above 350 K, then when a mixed CH_x/NH_y monolayer that has been e⁻ beam irradiated is annealed to various temperatures, cooled to 300 K, and then exposed to H₂, surface CN can be detected through the appearance of the aminocarbyne spectrum. Figure 2a shows a reference RAIR spectrum for aminocarbyne on Pt(111), where the peaks at 1328, 1566, and 3369 cm⁻¹ are due to ν(CN), δ(NH₂), and ν(NH), respectively. Figure 2b shows a RAIR spectrum for the case when 0.2 L of NH₃ and 0.2 L of CH₃I are irradiated with 100 eV electrons, annealed to 500 K, cooled to 300 K, and exposed to 10 L of H₂. Although much weaker, the peaks due to aminocarbyne are clearly observed. We found that brief anneals to temperatures lower than 500 K did not yield aminocarbyne RAIRS peaks. A peak is also observed in Figure 2b at 3310 cm⁻¹, which we assign to the NH stretch of surface NH formed by hydrogenation of the excess N_{ads} atoms that remain on the surface after the C–N coupling reaction. The formation and surface properties of NH will be discussed in detail

elsewhere.¹⁶ The assumption that the surface iodine plays no role in the reaction is confirmed by observation of CNH₂ with RAIRS in experiments in which surface carbon is prepared by annealing CH₃I to 800 K, which desorbs I but not C.^{7b} As further evidence for the insignificance of the surface iodine, we have found that surface CN can also be produced from the reaction of ethylene and N atoms, a reaction that was also observed in a secondary ion mass spectrometry study on Rh(111).¹⁷ Since we observe CN formation under conditions where none of the possible CH_x (*x* = 1, 2, 3) and NH_y (*y* = 1, 2) can exist, the C–N coupling reaction must occur between atomic C_{ads} and N_{ads} species.

Although our results reveal key details of the C–N bond coupling mechanism, many important issues remain unclear. For example, the maximum amount of HCN desorption that could be achieved is substantially less than the amount that desorbs following dissociative HCN adsorption. We found that the amount of CN reaches a maximum for low initial CH₃ coverages and that unreacted N atoms (as detected by RAIRS through the formation of NH upon H₂ exposure, as in Figure 2b) remain on the surface even when carbon is in excess. This suggests that competing with CN formation are reactions which convert C atoms into an unreactive form. This behavior is in good agreement with previous model reactor studies of HCN synthesis from ammonia and methane where it was found that surface carbon acts as both a reactant and a catalyst poison.^{2c}

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