

Supporting Information

Reaction pathways for HCN on transition metal surfaces

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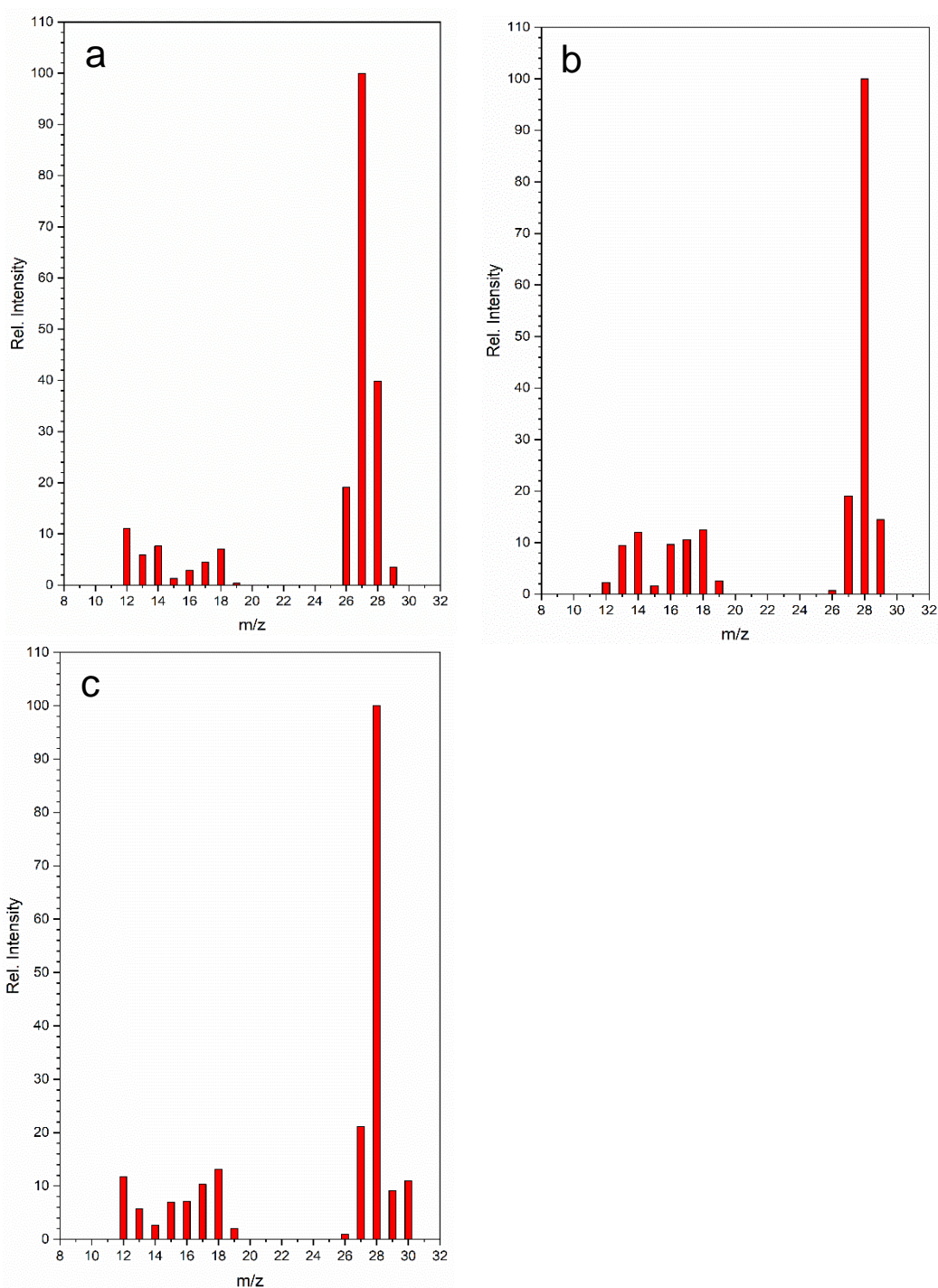


Figure S1: Mass spectra of 5.0×10^{-8} Torr of $\text{H}^{12}\text{C}^{14}\text{N}$ (a), $\text{H}^{13}\text{C}^{14}\text{N}$ (b), and $\text{H}^{12}\text{C}^{15}\text{N}$ (c). The synthesized products were determined to be pure by comparing the relative intensity of mass number 26 for $\text{H}^{12}\text{C}^{14}\text{N}$ (27 for the heavier isotopes) with that of the electron impact mass spectrum of HCN in the NIST database. An intensity of 20% relative to the parent mass number (27 for $\text{H}^{12}\text{C}^{14}\text{N}$ and 28 for the heavier isotopes) agrees with the national standard indicating successful synthesis and purification of HCN.

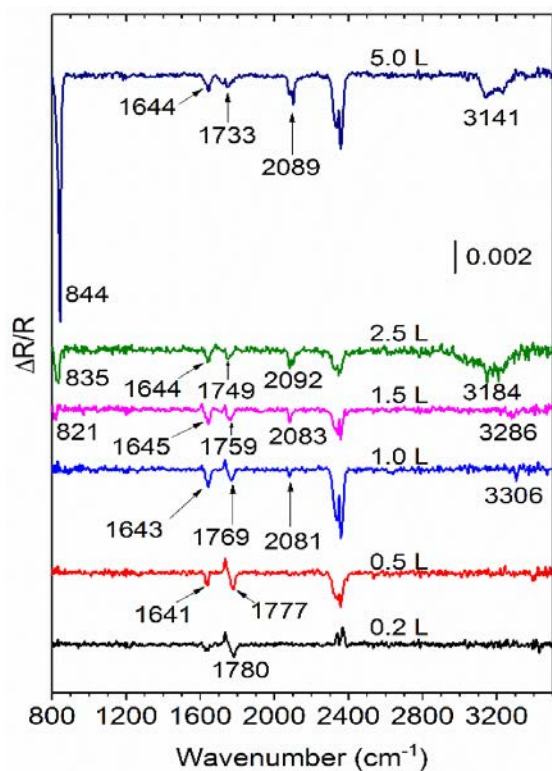


Figure S2: RAIR spectra of $\text{H}^{12}\text{C}^{14}\text{N}$ on Pd(111) taken at 90 K on clean Pd(111). The band at 821 cm^{-1} seen in the 1.5 L spectrum that shifts to 844 cm^{-1} for 5.0 L is due to the HCN bending mode, which only appears in the multilayer spectra. Solid HCN begins forming at exposures of 2.5 L as indicated by the broad C-H stretching mode at 3184 cm^{-1} .

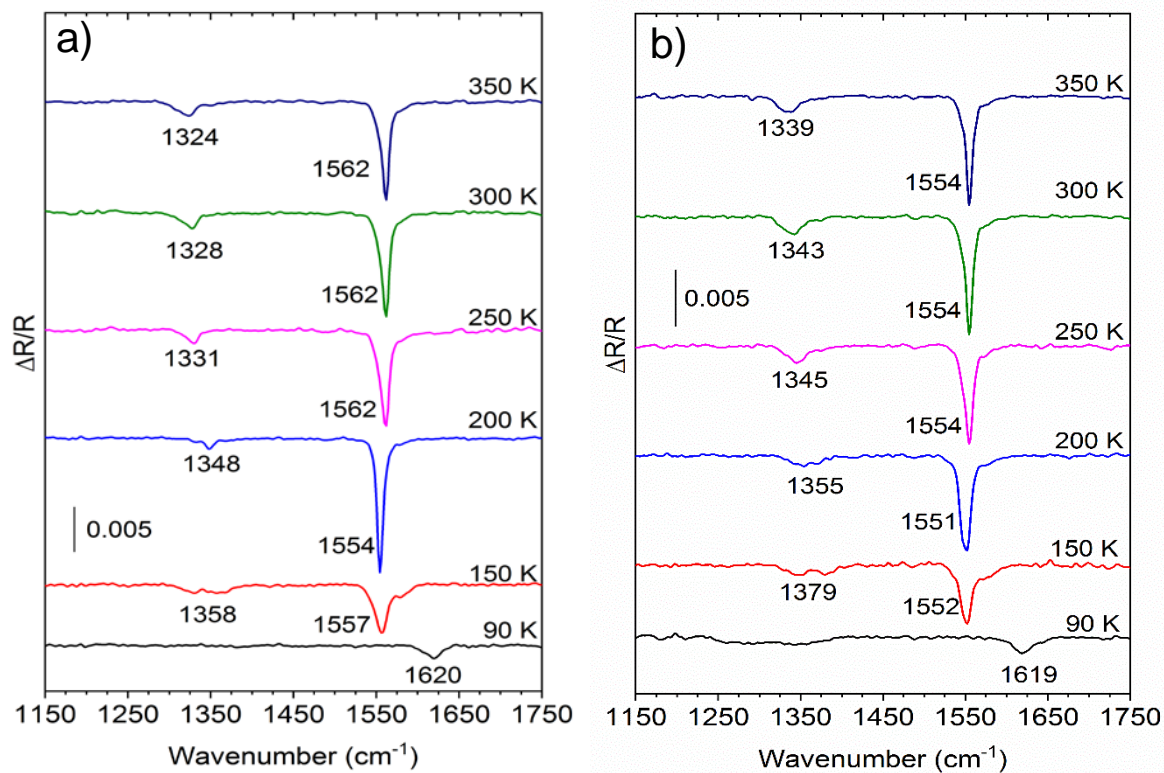


Figure S3: RAIR spectra of a) 1.0 L $\text{H}^{13}\text{C}^{14}\text{N}$ and b) 1.0 L $\text{H}^{12}\text{C}^{15}\text{N}$ on Pd(111) taken at 90 K after annealing for 1 minute at the indicated temperatures.

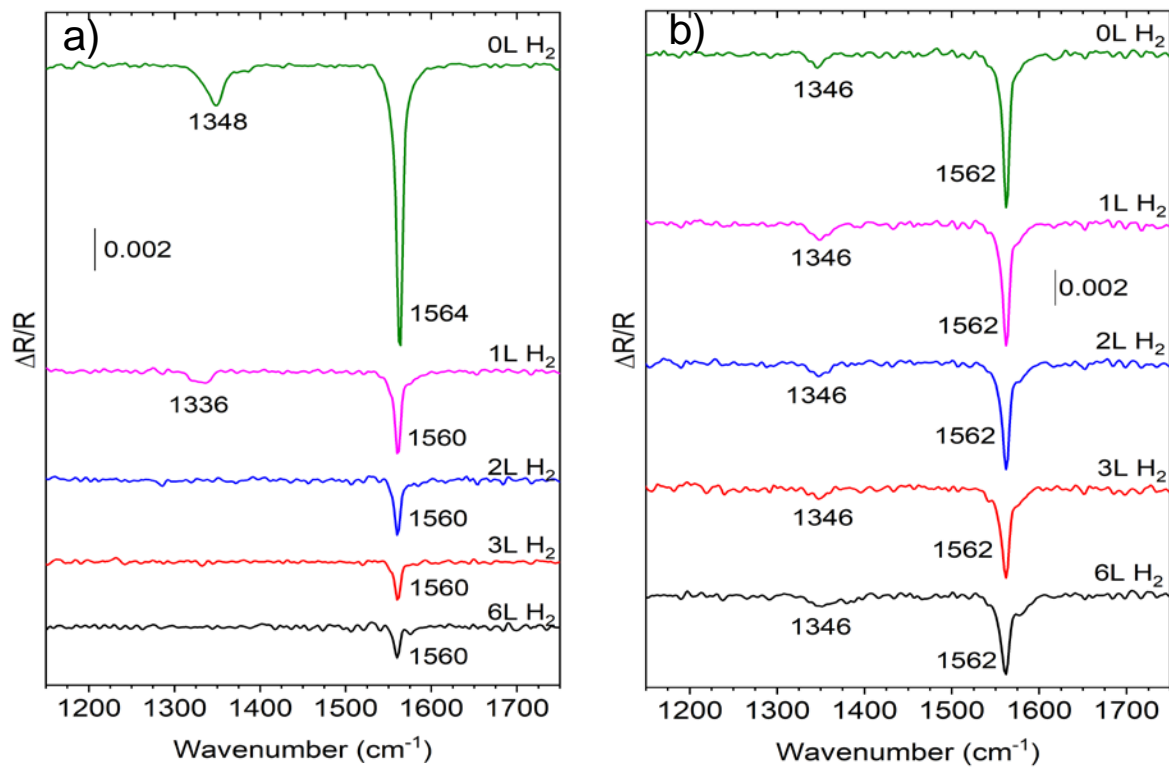


Figure S4: RAIR spectra taken at 90 K after annealing to 300 K for 1 min of $\text{H}^{12}\text{C}^{14}\text{N}$ on Pd(111) pre-exposed to H_2 (a) and exposed to H_2 after HCN exposure (b). Pre-exposure to H_2 reduced the amount of aminocarbene formed more than for post-HCN exposure to H_2 .

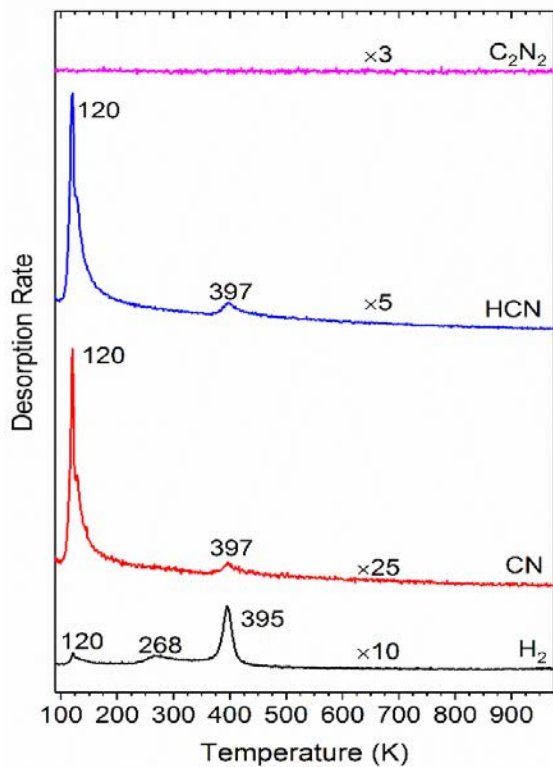


Figure S5: TPR spectra of 5.0 L HCN on Pd(111) taken from 90-1000 K at a heating rate of 1.5 K/s. Desorption of H₂ and HCN were observed at ~400 K. Although observed in other studies,^{1,2} C₂N₂ was not observed as a desorption product in this work.

Calculated adsorption energies of various fragments using different methods

Based on the adaptive summing method of Hensley et al.,³ when the GGA-RPBE ΔE_{ads} value for a gas molecule falls roughly below 70% of the corresponding value in optB86b-vdW, one may expect the contribution of vdW to the adsorption energy on a transition metal surface like Pd(111) to become significant. Table S1 lists the ΔE_{ads} of several surface species that may be referenced directly to stable gas-phase species. See Ref. 3 for definition of the parameters x and f . An adaptively weighted sum of GGA-RPBE and optB86b-vdW ΔE_{ads} is found to be on average more accurate than that calculated using either functional alone. When $f = 1$ (as is the case for all the organic species listed in Table S1), this sum consists entirely of the optB86b-vdW ΔE_{ads} . When $f = 0$, the sum consists entirely of the GGA-RPBE ΔE_{ads} . Thus Table S1 indicates that GGA-RPBE under-binds the organic species but is adequate for describing H adsorption, on Pd(111). Comparison with available literature data suggests this conclusion to be correct.

Table S1: DFT-calculated adsorption energies (ΔE_{ads} , in eV) of several molecular and atomic intermediates in HCN decomposition on Pd(111), and their associated adaptive summing parameters (x and f).

Species	ΔE_{ads}		ΔE_{ads}		ΔE_{ads} Exp. Lit.
	GGA-RPBE	optB86b-vdW	x	f	
HCN upright	0.00 ²	-0.56 ²	1.00	1.00	-0.39 ¹
HCN di-s	-0.47 ²	-1.29 ²	0.63	1.00	
(HCN) ₂ ^a	-0.15 ^{2,3}	-1.02 ^{2,3}	0.86	1.00	
CNH	-1.08 ²	-1.80 ²	0.40	1.00	
H	-0.39 ⁴	-0.57 ⁴	0.31	0.01	-0.44 ⁵

Each adsorbate is located on a (2×2) surface unit cell at 1/4 ML coverage. ΔE_{ads} is with respect to each adsorbate in gas phase and is non-ZPE corrected.

¹ From Ref. 2

² With respect to gas-phase HCN.

³ Per unit of HCN.

⁴ With respect to gas-phase H₂, per H atom.

⁵ From Ref. 4.

References

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2. X. Guo, A. Hoffman and J. T. Yates, *J. Phys. Chem.*, 1989, **93**, 4253-4258.
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