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Diimide formation on the Ni(100) surface

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Diimide (N_2H_2), an extremely reactive species, is observed as a gas phase product from the Ni(100) surface in the 200 to 450 K range during hydrazine thermal decomposition and during thermal desorption of predissociated ammonia. These results suggest that the primary mechanism for diimide formation is recombination of an adsorbed NH surface intermediate. The observation that diimide can be formed from predissociated ammonia illustrates that a nitrogen–nitrogen bond in the precursor is not required for diimide formation. Diimide formation from predissociated ammonia is enhanced by coadsorbed hydrogen, which we believe stabilizes NH on the Ni(100) surface. In addition, the direct decomposition of adsorbed N_2H_4 contributes to the production of diimide at 230 K.

Diimide, the parent of azo compounds, is of great interest to chemists because it is an important transient intermediate in both gas-phase reactions, and in the selective hydrogenation of multiple bonds in organic molecules. However, it was not until 1958 that diimide was first detected in situ during the discharge-induced decomposition of hydrazine in solution [1], because the reactivity of diimide makes its isolation difficult. Only recently has gas phase diimide formation been observed from a solid surface under UHV conditions. Our group has recently observed diimide formation during thermal decomposition of ammonia and hydrazine on polycrystalline Rh surfaces [2,3]. As part of a program to establish the generality of diimide formation, we have undertaken a study of diimide formation on the Ni(100) surface using hydrazine and predissociated ammonia as precursors.

Hydrazine adsorption and decomposition on single crystal metal surfaces has been characterized previously on Ir(111) [4], Rh(111) [5], Rh(100) [6], Fe(111) [7], Ni(111) [8], and Pt(111) [9] surfaces. Thermal decomposition studies on Rh(111), Rh(100), Pt(111), and Ni(111) surfaces suggest that hydrazine decomposes completely at submonolayer coverages on these surfaces. The pri-

mary gas phase products are N_2 , NH_3 , and H_2 . On these surfaces (except perhaps Pt(111)), the existence and importance of $NH_2(ad)$ and/or $NH(ad)$ intermediates is evident. Thermal decomposition of hydrazine also leads to diimide production on Rh foils [2,3], and possibly on the Pt(111) surface [9].

Ammonia adsorption and decomposition has been previously characterized on the Ni(100) [10], Ni(110) [11–14], and Ni(111) [15] surfaces. Nickel is a well-known ammonia decomposition catalyst [16]. However, several vacuum based surface studies have concluded that no significant thermal decomposition can be observed on either the Ni(111) [15] or Ni(110) surfaces [11,12] at temperatures below 300 K in an electron free environment. We believe that most of the ammonia decomposition observed in these studies is the result of electron irradiation. These ammonia results may also have substantial ramifications at elevated pressures and temperatures, because evidence for some degree of ammonia thermal decomposition clearly exists [13,17]. On the Ni(100) surface, molecular ammonia together with its decomposition products (NH_2 , NH , N) populate the surface at room temperature as evidenced by the XPS spectra [10].

The experimental apparatus utilized in this work has been described previously [3]. It consists of a stainless steel ultra-high vacuum (UHV) chamber in which the base pressure was 7.4×10^{-11} Torr. The system is also equipped with low-energy electron diffraction (LEED) optics, Auger electron spectroscopy (AES), and a multiplexed quadrupole mass spectrometer for temperature-programmed reaction spectroscopy (TPRS). The Ni(100) crystal was cleaned by argon ion bombardment and subsequent flashing to 1150 K; and its cleanliness was verified by Auger electron spectroscopy. The reactants (N_2H_4 and NH_3) were adsorbed at 90 K through a doser approximately 2 cm away from the Ni(100) surface. Special care was taken to ensure the minimum decomposition of N_2H_4 by evacuating and recharging the doser before each dose [18]. TPD data were taken with a linear temperature ramp of 5 K/s while the crystal is in line of sight with the mass spectrometer.

Fig. 1 presents the desorption spectra generated following the adsorption (at 90 K) of a submonolayer dose of hydrazine. At this dosage, N_2H_4 reacts completely on the Ni(100) surface to form NH_3 , N_2H_2 , H_2 , and N_2 . For coverages above one monolayer, a molecular sublimation peak is also identified for hydrazine at 170 K. The sharp ammonia, nitrogen, and diimide peaks at 230 K are believed to be the result of direct hydrazine decomposition, as in the case of hydrazine/Rh [3]. In the temperature range 300 to 520 K, the partially dissociated hydrazine species on the surface go through a dehydrogenation process, and produce gas-phase hydrogen as a result. At even higher temperature, the only product observed is molecular nitrogen formed between 750 and 1100 K. The broad diimide feature above the 230 K peak is quite interesting. This peak appears in the 350–400 K range at low coverages, and broadens to lower temperature range (200–450 K) at higher coverages. Eventually, a clear peak appears at 230 K with a high temperature shoulder extending to 450 K for coverages close to monolayer coverage of hydrazine. Based on these observations, we believe that second-order bimolecular reaction between adsorbed NH intermediates is the main mechanism responsible for

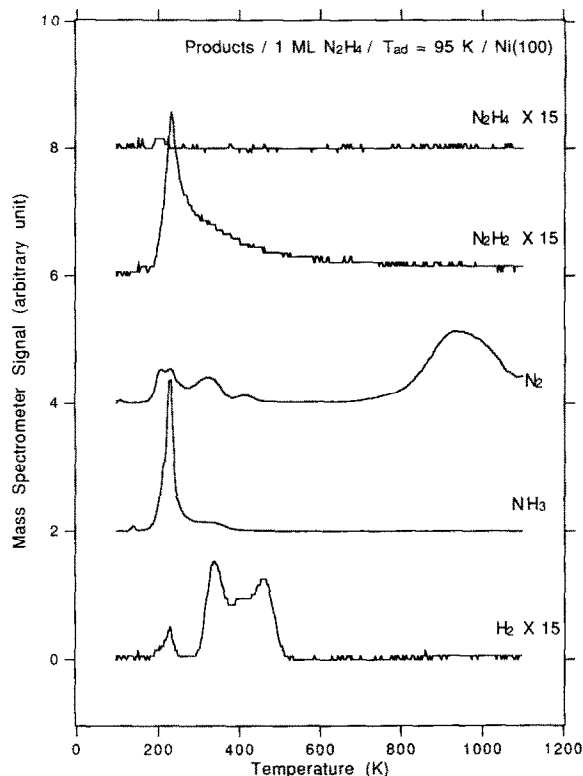


Fig. 1. Thermal desorption spectra of N_2H_4 on Ni(100). The spectra were taken in a single run of temperature-programmed reaction of N_2H_4 (submonolayer coverage) on the surface, with all the products monitored simultaneously. Here, the major products are N_2H_4 , N_2H_2 , N_2 , NH_3 , and H_2 .

producing diimide [18]. We propose that an important intermediate in this process is adsorbed imide (NH) which is formed by dehydrogenation of N_2H_4 . The adsorbed imide continues to react up to 450 K, suggesting that adsorbed imide is quite stable on the Ni(100) surface. Hydrazine-derived NH is known to be an important intermediate on Fe(111) [7], and Ni(111) [8] surfaces up to 400 K. Hydrazine-derived NH has also been observed on polycrystalline Rh [2,19], Al [20], Fe [21], Ir [22], W [23] and Mo [24] surfaces. In the 300 to 450 K temperature range, the imide intermediate appears to dominate diimide formation on Ni(100) surface. Above 450 K, we propose that NH dehydrogenates on the surface resulting in diminishing diimide yields from N_2H_4 .

Fig. 2 shows the temperature programmed reaction products from predissociated ammonia on the Ni(100) surface. For submonolayer coverages of NH₃, the major desorption peak is a molecular ammonia peak in the 180 to 400 K range. We also observe a small amount of hydrogen which desorbs at about 370 K. Diimide formation appears first at 350–400 K for low coverages of predissociated ammonia, and broadens to a lower temperature range (180–500 K) for higher coverages of predissociated ammonia. As in the case of hydrazine adsorption on the Ni(100) surface, we propose that the major mechanism for diimide formation is second-order combination of adsorbed imide intermediates. We believe that adsorbed imide intermediate (NH) is produced by electron

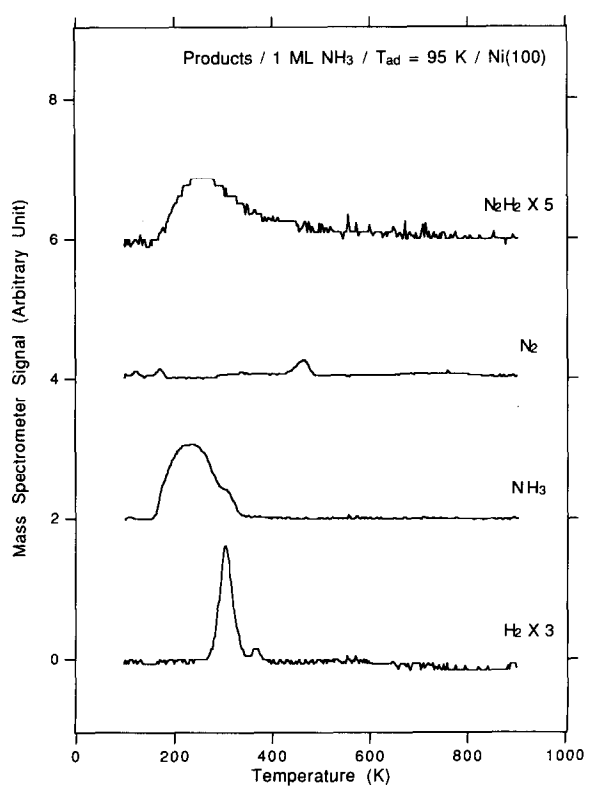


Fig. 2. Thermal desorption spectra of NH₃ on Ni(100). The spectra were taken in a single run of temperature-programmed reaction of NH₃ (submonolayer coverage) on the surface, with all the products monitored simultaneously. Here, the major products are N₂H₂, N₂, NH₃, and H₂. The peak at 450 K in the N₂ spectrum is likely due to CO contamination.

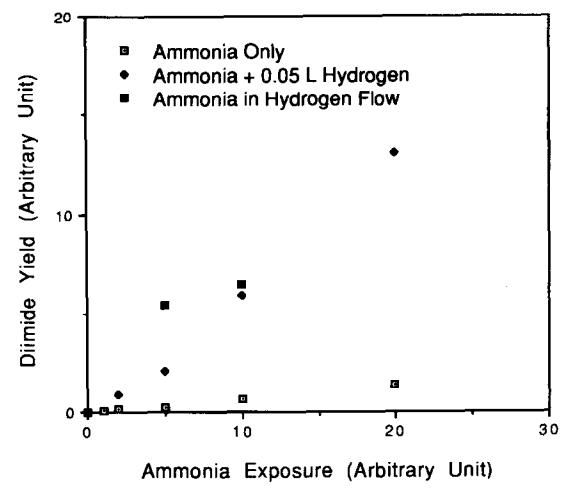


Fig. 3. N₂H₂ yield from submonolayer coverage of NH₃ on Ni(100), with and without coadsorbed hydrogen species.

bombardment of adsorbed ammonia and is stable through the 180–500 K temperature range. The existence of imide on Ni(100) was indeed verified by a XPS feature at 397.7 eV at room temperature [10]. Yates et al. have proved that ammonia is non-dissociative on the Ni(110) surface when free of electron bombardment [8]. The same is true on the Ni(111) surface where electron-induced decomposition of ammonia may contribute significantly to the formation of some intermediate species [6]. We, too, believe there is great possibility of electron beam induced ammonia decomposition on the Ni(100) surface.

Formation of N₂H₂ is appreciable from both N₂H₄ and predissociated NH₃ on the Ni(100) surface. In both cases, broad diimide peaks appear around 350–400 K at low coverages, and shift to lower temperature at higher coverages. However, ammonia is different from hydrazine in that it is a precursor which does not contain a nitrogen–nitrogen bond. Diimide formation from predissociated ammonia supports our contention that adsorbed NH is the primary surface intermediate responsible for diimide formation. The crucial step for diimide formation from both NH₃ and N₂H₄ is the formation of an adsorbed NH intermediate species and the bimolecular recombination of these species in the 200 to 450 K range. Above 450 K, NH dehydrogenates further

into $N_{ad} + H_{ad}$ on the surface, as indicated by the diminishing diimide yields from both N_2H_4 and predissociated NH_3 .

Diimide from predissociated ammonia is enhanced greatly by the coadsorption of hydrogen on the Ni(100) surface. As shown in the diimide yield curve (fig. 3), the yield of diimide from ammonia is increased significantly in the presence of post-adsorbed hydrogen or in a 10^{-7} Torr hydrogen flow. We believe that coadsorbed hydrogen stabilizes the NH intermediate, and therefore increases the surface concentration of imide in the hydrogen-deficient surface environment in the 200–450 K temperature range. This result is in good agreement with similar results from NH_3 on polycrystalline rhodium foil [2], and serves as further support for the importance of imide as an intermediate.

The diimide yield from N_2H_4 does not respond to the addition of hydrogen. We propose that substantial hydrogen coverages are present after adsorption of hydrazine because of substantial low temperature hydrazine decomposition. Therefore, the stability and recombination of adsorbed NH is not substantially affected by additional coadsorbed hydrogen. In addition, during hydrazine decomposition for coverages close to one monolayer, there is a second sharp diimide peak at 230 K which we believe is the result of diimide formed directly from hydrazine. This low temperature diimide is not affected by the coadsorbed hydrogen either.

In summary, diimide (N_2H_2) is observed as a gas phase product from the Ni(100) surface in the 200 to 450 K range during hydrazine thermal decomposition and during thermal desorption of predissociated ammonia. These results suggest that the primary mechanism for diimide formation is recombination of adsorbed NH surface intermediates. The observation that diimide can be formed from predissociated ammonia illustrates that a nitrogen–nitrogen bond in the precursor is not required for diimide formation. Diimide formation from predissociated ammonia is enhanced by the coadsorbed hydrogen which we believe stabilizes NH on the Ni(100) surface. In addition, the direct decomposition of adsorbed

N_2H_4 also contributes to the production of diimide at 230 K. Further spectroscopic characterization of this process will allow more detailed characterization of both the surface species and surface reactions that favor the diimide formation.

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