Thermal Chemistry of Hydrazine on Clean and Oxygen- and Water-Predosed Cu(110) Single-Crystal Surfaces

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Abstract

The chemistry of hydrazine on Cu(110) single-crystal surfaces was probed under ultrahigh vacuum (UHV) conditions by temperature-programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). Survey TPD experiments identified molecular nitrogen and ammonia as the main desorbing products from thermal activation of the adsorbate, but small amounts of diazene and $\text{NH}_2\cdot$ radicals were also detected. At saturation coverages N_2 production leads NH_3 desorption by approximately 10 K (with TPD peaks at 350 versus 360 K, respectively), indicating a preference for dehydrogenation over N–N bond scission steps, and additional nitrogen was seen at even lower temperatures (320 K) in experiments starting with even higher doses of hydrazine. On the other hand, the formation of NH_3 and $\text{NH}_2\cdot$, which desorb in a wide range of temperatures between approximately 300 and 700 K, dominates in experiments with low N_2H_4 doses, presumably because a stronger interaction of the N–N bond with the metal in the flat adsorption geometry expected at such low coverages. Adsorption at room temperature seems to also facilitate the dissociative adsorption, albeit via dehydrogenation

steps that lead to the subsequent production of more significant amounts of diazene and of molecular hydrogen (in addition to N_2 , NH_3 , and $\text{NH}_2\cdot$). Preadsorption of oxygen on the Cu(110) surface helps stabilize the hydrazine, increasing its desorption temperature and helping with the low-temperature (320 K) production of N_2 . Coadsorption of hydrazine with water leads to facile proton exchange, as indicated by the production of NH_2D in TPD experiments with $\text{N}_2\text{H}_4 + \text{D}_2\text{O}$. This isotope scrambling must occur at cryogenic temperatures, because all water desorbs from the surface below 200 K and no other changes in surface chemistry are observed after that. The implications of all this chemistry to practical applications that may use hydrazine in surface reactions with copper, including its use as a reducing agent in atomic layer deposition (ALD) processes, are discussed.

Keywords: Hydrazine, Copper Single-Crystal Surface, Predosed Oxygen, Water, Thermal Programmed Desorption, X-Ray Photoelectron Spectroscopy, Diazene.

1. Introduction

The thermal chemistry of hydrazine on metal surfaces has elicited some attention over the years in connection with a number of applications. Early work used hydrazine as a convenient precursor for the formation of $\text{NH}_2(\text{ads})$ and $\text{NH}(\text{ads})$ surface species, likely intermediates in key catalytic reactions such as ammonia synthesis, and the formation of such intermediates was indeed corroborated by using several surface-sensitive techniques. For instance, Grunze speculated, based on UV (UPS) and X-ray (XPS) photoelectron spectroscopy data, that N_2H_4

dissociation on Fe(111) surfaces leads to the formation of $\text{NH}_2(\text{ads})$ species at 220 K [1], and Menzel and coworkers proved convincingly, by using a combination of high-resolution electron loss spectroscopy (HREELS), temperature programmed desorption (TPD), low-energy electron diffraction (LEED), and work function measurements, that a similar sequence takes place on Ru(001) [2]. In contrast, studies on Pt(111) indicated that hydrazine decomposition occurs via N–H, not N–N, bond breaking, to produce N_2 intramolecularly and ammonia via hydrogenation of N_2H_y surface fragments [3-5]. The chemistry on Rh(100) [6] and Rh(111) [7; 8] seems to fall in between that on Fe and Pt, with evidence for both N–N dissociation and ammonia production as well as N–H bond scission steps, in the case of Rh(111) to produce diazene. Diazene, which is an interesting species in its own right because, as the parent of azo compounds, is an important transient intermediate both in gas-phase reactions and in the selective hydrogenation of multiple bonds in organic molecules, was also detected from activation of hydrazine on Ni(100) [9]. More esoteric mechanisms, including the production of molecular nitrogen via an intermolecular reaction involving two hydrazine adsorbates, have been proposed as well [10; 11].

Another early use of hydrazine has been as a source of nitrogen atoms to prepare surface nitrides. In connection with that application, Kiskinova and Goodman reported the successful formation of an atomic nitrogen surface layer on a Ni(100) single-crystal surface via the activation of hydrazine at 600 K, at which point molecular hydrogen evolves into the gas phase [10]. On the other hand, Gland and coworkers determined, using vibrational spectroscopy, that hydrazine decomposition on Ni(111) results in the formation of a $\text{NH}(\text{ads})$ stable intermediate between 285 and 365 K [12]. More commonly, studies on surface nitridation have been carried out on semiconductor surfaces such as Si(111)-(7 × 7) [13] and Si(100)-(2 × 1) [14]. In those cases,

dehydrogenation steps were shown to precede the scission of the N–N bond, even if ultimately both types of reactions were proven possible, and the formation of a Si_3N_4 layers was evidenced.

A third application of hydrazine in surface science and catalysis is as a reactive and carbon- and oxygen-free source of hydrogen [15-18]. Hydrazine may be used as a monopropellant, in which case decomposition is typically promoted by iridium dispersed on a granular alumina support [19; 20], and also in fuel cells [21; 22], for which a corrosion-resistant metal such as copper is highly desirable [23]. More recently, hydrazine has been proposed as an effective reducing agent in materials science synthesis. For instance, the selective reactivity of hydrazine as a reducing agent with several capping agents in colloidal solutions has been used to design processes for the formation of size- and shape-controlled metallic nanoparticles [24-27]. Hydrazine has also been introduced as both a reducing agent and a source of nitrogen for the atomic layer deposition (ALD) of thin films on metal and metal nitride surfaces [28; 29].

Our interest in the surface chemistry of hydrazine on Cu surfaces derives primarily from a new report on the use of such reducing agent, in combination with formic acid, in the ALD of copper films [30; 31]. One of our long-term goals is to develop a mechanistic understanding of how such co-reactants operate in conjunction with metalorganic precursors in ALD [32; 33]. We have also extended our work to probe the interaction of hydrazine with atomic oxygen and with water on the Cu surface in order to acquire additional insights into the surface chemistry related to some of the other catalytic systems mentioned above, including hydrogen production, which apparently works in gas phase but not in solution [16; 17]. Interestingly, there is virtually no experimental work on the thermal chemistry of hydrazine on copper surfaces (none, to the best of

our knowledge, other than a brief early mention on copper films [34]), yet there have been extensive discussion in the literature about this system from a computational point of view [35-39]. The activation energy for the scission of the N–N bond in Cu(111) was estimated at approximately 57 kJ/mol, reasonably low even if higher than on Fe(110), Co(0001), or Ni(111) [39], and the resulting NH₂(ads) dissociated species were found to be thermodynamically more stable than molecularly adsorbed N₂H₄ [37]. Unfortunately, most quantum mechanics studies on copper to date have focused on the initial adsorption step of N₂H₄ on the surface, and do not provide information on the relative reactivity of the N–N versus N–H bonds or on the relative stability of the different potential surface intermediates. In our experimental results, we find that the main desorbing products from thermal activation of hydrazine adsorbed on Cu(110) are N₂, and NH₃, indicating that both types of bond scissions are feasible on that surface. More details follow.

2. Experimental Details

All of the experiments reported here were performed in a stainless-steel ultrahigh vacuum (UHV) chamber turbopumped to a base pressure in the low 10⁻¹⁰ Torr range and equipped with an Extrel quadrupole mass spectrometer for TPD experiments and a 50-mm radius VSW hemispherical electron-energy analyzer and an aluminum anode (hν = 1486.6 eV) for X-ray studies, as described elsewhere [40-42]. A Cu(110) single crystal, a disk 10 mm in diameter and 1 mm in thickness, was mounted on a concentric manipulator via thin tantalum wires wedged into side slots made in the crystal for this purpose and fixed to the ends of copper vacuum

feedthroughs in order to be able to cool down to ~ 80 K and to resistively heat to up to 1100 K. The temperature was measured by using a K-type thermocouple wedged into a hole drilled on the side of the crystal, and controlled using a homemade proportional-integral-derivative (PID) circuit.

For the TPD experiments, the ionizer of the mass spectrometer is encased inside a cylindrical stainless-steel box with a 7-mm-diameter front aperture to selectively probe the gases that desorb from the crystal surface. The mass spectrometer is interfaced to a personal computer in a set up capable of following the evolution of the partial pressures of up to 15 different masses in a single TPD run. A constant heating rate of 5 K/s was employed. For the XPS experiments, the electron-energy analyzer was set to a 50-eV constant pass energy for an overall resolution of approximately 1.5 eV FWHM and an accuracy in peak position of approximately 0.1 eV. Binding energies (BEs) are all referenced to a value of 932.4 eV for the Cu 2p_{3/2} peak of metallic copper [43]. The peak areas in Figure 7 were converted into monolayers (1 ML = 1 surface species per exposed Cu atom) based on the intensities of the Cu 2p_{3/2} peak for the clean Cu(110) surface and reported relative sensitivities for the different photoelectrons [44]. Because of the approximations made (layered distribution of elements, etc.), the absolute values may not be fully reliable, but our focus is on the relative signal intensities, used to estimate the extent of the surface chemistry observed in each temperature range.

The surface of the crystal was cleaned before each experiment by sequential cycles of Ar⁺ ion sputtering and annealing until it was deemed clean by XPS. Anhydrous hydrazine was purchased from Sigma-Aldrich (reagent grade, 98% purity), and distilled in situ within the gas

manifold via several freeze-pump-thaw cycles right before use. Perdeuterated water (D_2O) was also obtained from Sigma-Aldrich (99.9% isotope purity), and purified the same way. Oxygen gas was purchased from Liquid Carbonic (Research Purity, >99.995%) and used as supplied. Dosing of the sample was done by backfilling of the chamber using leak valves, and is reported in Langmuirs ($1\text{ L} = 1 \times 10^{-6}\text{ Torr sec}$), uncorrected for differences in ion gauge sensitivities. The pressure in the main UHV chamber was measured by using a nude ion gauge.

3. Results

The thermal chemistry of hydrazine on clean Cu(110) was first probed by TPD. Figure 1 shows typical data, in this case for a 4.0 L dose at 140 K, from surveying experiments designed to identify the main desorbing products and their basic temperature profiles. In addition to molecular desorption, which is seen in most traces and is best identified by the sharp peak around 170 K in the 32 amu trace, the main species evolving into the gas phase are manifested by mass spectrometry signals in the spectra for 16, 17, and 28 amu. The 28 amu signal shows an intense peak at approximately 350 K corresponding to the desorption of N_2 , as corroborated by the weaker peak with similar shape and position in the 14 amu trace (atomic nitrogen) and by the absence of any signal in the 12 amu data (ruling out any carbon-containing species). The traces for 16 and 17 amu look quite similar, with an early peak at ~360 K followed by a broad feature covering the temperature range from 300 to approximately 700 K, and are both associated mainly with ammonia desorption (any interference from water is ruled out by the absence of signal in the 18 amu trace). There is a slight signal intensity excess in the 16 amu trace not

accounted for by the intensity in the 17 amu data around the broad feature on the high-temperature side, indicating the desorption of additional species containing NH_2 moieties, most likely $\text{NH}_2\cdot$ radicals, and also a weak (but reproducible) broad desorption between approximately 250 and 400 K in the 29 amu trace, which strongly suggests the formation of a small amount of diazene ($\text{HN}=\text{NH}$, or N_2H_2). Interestingly, there is virtually no H_2 production in this system: a small amount of H_2 is perhaps detected around 350 K, but if so the signal is within the experimental noise. There may be some additional N_2 desorption seen in the 28 amu at high temperatures, at about or above 900 K, which could correspond to recombination of residual atomic nitrogen from full dehydrogenation of $\text{NH}_x(\text{ads})$ species, but that could also be the result of an experimental artifact.

Figure 2 summarizes the desorption data for the main species detected from thermal activation of N_2H_4 on Cu(110) as a function of exposure. The left panel, which reports molecular desorption (as followed by the signal for 32 amu), only shows one low temperature peak starting at 170 K and shifting slightly to higher temperatures with increasing doses that is most likely associated with condensed hydrazine. Notice that molecular desorption only starts at N_2H_4 exposures of approximately 4 L, indicating that the adsorbates at low coverages undergo total thermal decomposition. In terms of the N_2 desorption reported in the second panel of Figure 2, the main peak seen at 350 K is not seen at low coverages but fully develops by 4.0 L, and remains invariant in terms of both intensity and position upon further increases in hydrazine dose. In addition, a second feature develops around 330 K by 15 L. It appears that crowding of the surface helps with the dehydrogenation of N_2H_4 to N_2 , perhaps by forcing the chemisorbed hydrazine molecules into a perpendicular adsorption configuration that maximizes N–H

activation. Less likely, that second TPD feature may be the result of an intermolecular reaction between species in the first and second monolayers, as suggested for other metals in the past [10; 11].

The evolution of the TPD for ammonia, which was followed by recording the signal for 17 amu, is shown as a function of hydrazine initial exposure in the third panel of Figure 2. Ammonia is the main product at low coverages, but its formation is partially suppressed as the hydrazine dose is increased. Below 3 L, most of the NH_3 is detected at high temperatures, in two broad features peaking at around 440 and 550 K, respectively. However, by 4 L those TPD features decrease significantly in size, and are replaced in part by a better-defined new feature at 360 K, a temperature a few degrees higher than that of the N_2 TPD peak. The evolution of molecular nitrogen and ammonia in this early temperature regime may be connected, but there is a slight delay in the production of the latter with respect to the former, indicating a preference for dehydrogenation steps before any N–N bond scission takes place. It is also interesting to note that the hydrogen atoms released by the N_2 production seem to all be consumed by the production of ammonia (which may take place via recombination of $\text{NH}_2(\text{ads})$ with $\text{H}(\text{ads})$), because no H_2 evolution is seen in the TPD. For hydrazine doses below 4 L, where virtually no molecular nitrogen desorption is detected, ammonia production is accompanied by the release of $\text{NH}_2\cdot$ species, as clearly seen in the traces for 16 amu after correcting for the cracking pattern of NH_3 (Figure 2, last panel). It is likely that further dehydrogenation, to $\text{NH}(\text{ads})$ and $\text{N}(\text{ads})$, takes place in this low-dose regime as well, since such steps are needed to account for the stoichiometry implied by the production of ammonia at these low surfaces coverages of hydrazine. No $\text{NH}_2\cdot$ desorption is seen above 4 L.

More extensive hydrazine thermal activation can be induced by carrying out the adsorption at higher surface temperatures. Figure 3 displays the data from a TPD obtained after dosing 10 L of N_2H_4 onto a Cu(110) surface held at 300 K. Several significant differences are observed. For one, most of the chemistry observed in the TPD peaks occurs at higher temperatures (compared to what is reported in Figures 1 and 2), presumably because extensive dehydrogenation takes place during the room-temperature uptake leading to more strongly bonded surface species. All ammonia, $\text{NH}_2\cdot$, and molecular nitrogen are produced, almost congruently, in two temperature peaks at approximately 430 and 470 K. Moreover, some H_2 is now seen to desorb in the same temperature range, and diazene is clearly detected in the 29 amu trace, at slightly lower temperature than the other products.

The effect of coadsorbed water and/or coadsorbed oxygen on the thermal chemistry of hydrazine on Cu(110) was tested next. The TPD traces for a 5.0 L N_2H_4 dose on the appropriate surfaces are reported in Figure 4. The first panel corresponds to the chemistry on the clean surface, and follows the trends discussed above: the main desorbing species are molecular N_2H_4 at 175 K, N_2 production at 350 K, and NH_3 desorption in a well-defined peak at ~ 360 K and in a long high-temperature tail extending from 400 to 700 K. The second panel displays the results from an experiment carried out on a surface predosed with 0.5 L of D_2O at low temperatures. It is well known that water does not bond strongly to clean copper and desorbs from the first monolayer at about 165 K and from multilayers around 155 K (Figure 5, left panel) [45]. It appears that coadsorption with hydrazine does not alter that chemistry, since the same molecular desorption is seen in that case (Figures 4, second panel, and 5, left panel), and since no other (deuterated)

water desorption peaks are seen in the TPD data. Moreover, the production of N_2 and ammonia follow the same kinetics as on the clean copper, as expected if all the water desorbs at low temperatures. On the other hand, a significant amount of NH_2D is seen in these experiments. The most likely explanation is that the coadsorbed N_2H_4 and D_2O undergo isotope scrambling, possibly via hydrogen bonding, at very low temperatures, before the water desorbs. A small peak is also seen at 360 K in the 2 amu trace, but it is not clear if this is due to H_2 production, or, more likely, to cracking of NH_2D in the mass spectrometer.

Clean copper surfaces are fairly unreactive toward thermal activation of adsorbed acidic or basic organic molecules such as water, formic acid or ammonia, but can be activated via the addition of small amounts of atomic oxygen [42; 45; 46]. The third panel in Figure 4 shows the TPD data obtained from a surface dosed with 5.0 L of N_2H_4 after predosing it with 0.1 L of O_2 (all at 140 K). A few significant differences are seen when comparing with the traces from the clean Cu(110) surface. First, oxygen seems to stabilize molecular adsorption: in addition to the sharp 170 K peak in the 32 amu trace due to desorption of condensed N_2H_4 , significant additional intensity is seen all the way to ~500 K, with a peak at 260 K. Moreover, the presence of oxygen on the surface seems to facilitate the low-temperature (320 K) N_2 peak, which is seen on the clean copper surface only after much higher N_2H_4 doses. Additional nitrogen is still produced at 350 K, and ammonia detected at 360 K and then in a range extending to ~700 K, as on the clean substrate. Lastly, the coadsorption of all three water, oxygen, and hydrazine reactants results in TPD equivalent to the sum of the other data discussed above (Figure 4, right panel). Water adsorption is stabilized by the coadsorbed oxygen, leading to a broader multippeak feature below 200 K, as also seen with the two adsorbates alone (Figure 5, right panel). However, no water

production from OH(ads) recombination around 280 K is seen in our example in Figure 4 (with hydrazine), as it occurs with coadsorbed O(ads) and OH(ads) alone (Figure 5, right panel) [45]. There is also no water retention on the surface above 300 K, at which point only the chemistry of hydrazine coadsorbed with oxygen is observed, namely, N₂ production at 320 and 350 K, and ammonia formation at 360 K and then in a broad feature up to 700 K. Once again, NH₂D from low-temperature isotope exchange with D₂O is detected, as in the case with N₂H₄ + D₂O in the second panel of Figure 4, and a peak is also observed in the 2 amu trace. No new chemistry was seen as a product of any unique synergy among all three adsorbed species.

Finally, the reactivity of N₂H₄ on clean and oxygen-treated Cu(110) surfaces was investigated further by using XPS. The relevant data are reported in Figure 6 in the form of N 1s (two left panels) and O 1s (right panel) peaks as a function of annealing temperature for 5.0 L of N₂H₄ dosed on clean (left panel) and oxygen-predosed (two right panels) surfaces, and a summary of the relative peak areas and XPS peak positions is provided in Figure 7. The XPS results are in general consistent with the conclusions derived from the TPD data. First, a N 1s peak for hydrazine multilayers condensed at low temperatures is seen at 400.6 eV binding energy, a value within the range of those reported previously for this compound in the literature [1; 3; 6; 14; 34; 47-49]. In addition, after molecular desorption below 200 K, the main changes are seen between 300 and 400 K in the form of a reduction in N 1s XPS peak intensity and a peak shift, correlating with the evolution of N₂, NH₃, and NH₂· seen in the TPD in the same temperature range (Figures 1, 2, and 4). A slow N 1s intensity decrease is seen up to that point, between 200 and 300 K, possibly a reflection of the slow desorption of N₂H₄ and N₂H₂ in that temperature range. In the end, after heating to 400 K, only a weak N 1s XPS feature centered at 401.2 eV remains,

corresponding to an estimated coverage of less than 0.04 ML, or less than 10% of the total nitrogen detected at the lowest temperature (150 K).

The XPS data for the adsorption of hydrazine on oxygen covered Cu(110) surfaces follow in general the same trends as on the clean copper, with a couple of noticeable exceptions, namely: (1) the N 1s XPS binding energies are all red-shifted by about 0.5 eV, presumably because of the increased electron density on the surface provided by the coadsorbed oxygen atoms; and (2) the changes in N 1s XPS peak intensities are seen earlier than on the clean substrate, when heating from 300 to 350 K versus when going from 350 to 400 K, presumably because the new 320 K N₂ desorption that takes place according to the TPD data (in addition to the feature seen on all surfaces at 350 K, Figure 4).

Regarding the evolution of the O 1s XPS signal seen upon thermal annealing of the N₂H₄/O/Cu(110) surface, an initial signal decrease is seen between 150 and 200 K. This is most likely due to desorption of coadsorbed water from the background, which may be enhanced by the coadsorbed hydrazine: the original O 1s XPS peak before hydrazine dosing corresponds to only about 0.1 ML of atomic oxygen on the surface (as opposed to the 0.15 ML measured at 150 K), and the additional intensity, which is lost again upon heating to 200 K, is centered at binding energies around 531.0 eV, as expected for condensed water. Between 200 and 250 K, the O 1s XPS peak shift considerably, from 529.9 to 530.8 eV, a change that we attribute to the formation of surface hydroxy (OH) groups via hydrogen extraction from the adsorbed hydrazine, in a similar fashion as also reported with a number of amines [50; 51] and alcohols [52]. That transformation is complete by 300 K, but an additional, subtler, change occurs between 300 and

400 K, a temperature range where the O 1s XPS peak position drifts from 530.8 to 531.2 eV without changing in total intensity. This is the regime where ammonia evolves into the gas phase and other dehydrogenated species likely form on the surface, which suggests that the surface oxygen atoms may intervene in the associated hydrogen transfer steps and perhaps retain some of the H atoms in the form of additional OH(ads) species. Certainly, the O 1s XPS peak obtained at 400 K is sharper than those seen at 300 and 350 K, reflecting the hydrogenation of some of the unreacted surface oxygen groups.

One important observation from the XPS data is that in all cases the N 1s XPS peaks shift to higher binding energies with increasing annealing temperatures (Figures 6 and 7). In general, this could be explained by the more positive charge expected in the more dehydrogenated species, either $\text{NH}_x(\text{ads})$ or $\text{N}_2\text{H}_y(\text{ads})$, that form on the surface upon thermally activated dehydrogenation, but the trend is opposite to those reported for hydrazine on most other metal surfaces. For instance, Grunze observed that, on Fe(111), heating up adsorbed hydrazine from 220 to 300 K leads to a shift in N 1s XPS binding energy from 400.2 to 396.6 eV, a value they ascribed to adsorbed atomic nitrogen [1]. On aluminum films, Roberts and coworkers saw similar changes, from 400.3 eV at 85 K, to 399.5 eV at 290 K, presumably because of the formation of $\text{NH}_2(\text{ads})$, and to 398.4 eV at 390 K, perhaps from $\text{NH}(\text{ads})$ or $\text{N}(\text{ads})$ [48]. Finally, the group of White reported that on Rh(100) the initial N 1s XPS peak for N_2H_4 adsorbed at low temperatures, centered at 400.1 eV, shifts to 397.5 eV at 530 K, corresponding to the formation of atomic nitrogen [6]. The one clear exception is the work of Alberas et al., who on Pt(111) reported the development of a new peak at 401.5 eV upon heating adsorbed hydrazine to 200 K (the peak for the original adsorbed hydrazine was seen at 400.2 eV) [3]. Their explanation for

this blue shifts in the N 1s XPS peak, which we think also applies to our Cu(110) system, is that the adsorbed hydrazine decomposes on the Pt (and Cu) surface primarily via dehydrogenation to form $\text{N}_2\text{H}_y(\text{ads})$ species, not by scission of the N–N bond to produce $\text{NH}_x(\text{ads})$ moieties as on the other metals. In support of this interpretation, it should be mentioned that the N 1s XPS peak reported for azomethane ($\text{CH}_3\text{N}=\text{NCH}_3$) adsorbed on Cu(110) is centered at 401.4 eV [53], the same value we see for hydrazine on clean Cu(110) after heating to 400 K. It may be that the surface species surviving on the Cu(110) surface above 400 K is chemisorbed diazene ($\text{HN}=\text{NH}$).

4. Discussion

TPD and XPS data has been provided here in support of our proposal for the mechanism of the thermal chemistry of hydrazine on clean and oxygen- and water-predosed Cu(110) single crystal surfaces. The main gas-phase products resulting from heating up N_2H_4 adsorbed on clean Cu(110) are nitrogen and ammonia, but small amounts of diazene (N_2H_2) and $\text{NH}_2\cdot$ radicals are detected as well. Consequently, it can be said that the copper surface promotes the scission of both N–H and N–N bonds in the original reactant. However, although these two families of reactions compete, the preference for one over the other is also clear and changes with initial coverage.

At low coverages, after exposures below 4.0 L, very little N_2 production is seen in the TPD data and the main products are NH_3 and $\text{NH}_2\cdot$, which evolve in a wide range of temperatures starting

at about 300 K and maximizing in rate at approximately 440 and 550 K. This suggests that adsorption of hydrazine is strong at low coverages, and leads predominantly to the dissociation of N–N bonds at relatively high temperatures. Nevertheless, ammonia production requires a source of atomic hydrogen, so the concomitant dehydrogenation of other adsorbed fragments to $\text{N}_2\text{H}_y(\text{ads})$, $\text{NH}(\text{ads})$ and/or $\text{N}(\text{ads})$ is likely. The ejection of $\text{NH}_2\cdot$ radicals, on the other hand, takes place with retention of the original stoichiometry, and may occur via direct N–N bond scission in molecules adsorbed at an angle from the surface plane.

At coverages near or above saturation, on the other hand, the selectivity of hydrazine decomposition on Cu(110) changes, and the conversion starts at lower temperatures and becomes dominated by N–H bond-breaking steps. Several pieces of information point to this switch: (1) the evolution of molecular nitrogen becomes dominant, seen in the TPD traces first by the appearance of a peak at 350 K and later, at higher coverages, by the growth of a second feature at even lower temperatures, approximately 330 K; (2) although ammonia is still produced at high coverages, the main peak lags that of N_2 production, peaking at 360 K (there is also additional NH_3 evolution until ~ 700 K); (3) the relative yields of molecular nitrogen versus ammonia in the TPD traces evolve from the predominance of ammonia at low coverages to a preference for nitrogen at saturation; (4) desorption of a small amount of diazene is seen between 250 and 400 K in the TPD data, and that product only requires dehydrogenation steps; and (5) the shifts of the N 1s XPS peaks toward higher binding energies with increasing surface temperatures are consistent with dehydrogenation steps and with the formation of chemisorbed diazene, and inconsistent with the creation of $\text{NH}_x(\text{ads})$ species. The relative inability of copper to activate the N–N bond in hydrazine compared to other transition metals is consistent with the detection of

$\text{NH}_x(\text{ads})$ surface species in most other surfaces studied to date [1; 6; 48] and also with the trend for the activation energies for N–N bond breaking estimated by DFT calculations [39], but not with the theoretical prediction that N–N bond breaking should dominate over molecular adsorption on copper [37]. Unfortunately, no theoretical study has yet addressed the issue of relative reactivity of N–H versus N–N bonds in hydrazine chemisorbed on transition metals directly.

Copper surfaces are known to be relatively inactive, especially towards the thermal activation of alcohols [54], organic acids [42; 52], or bases [46; 51]. The addition of small amounts of oxygen has been shown to increase that reactivity, by facilitating deprotonation via the formation of surface hydroxy groups. This chemistry was probed here with hydrazine. It was found that, indeed, coadsorbed oxygen stabilizes the chemisorption of N_2H_4 , and, perhaps more importantly, helps promote dehydrogenation steps. The latter is indicated by the development of a new N_2 TPD peak at 320 K (Figure 4, second panel), the same feature that is seen on the clean copper surface only at higher coverages (Figure 2). It could be thought be that the new TPD feature is simply the result of surface crowding, but hydrogen transfer steps are also indicated by the shifts seen in the O 1s XPS signal after heating to high temperatures due to the formation of the $\text{OH}(\text{ads})$ species expected from hydrogen abstraction from the hydrazine (Figures 6 and 7). In terms of reactions with coadsorbed water, the deuterium labeling TPD experiments presented in Figure 4 (using D_2O) clearly show incorporation of deuterium into the ammonia made from hydrazine. That exchange is likely to occur at low temperatures, because all water desorbs from the surface below 200 K, even when oxygen is added to provide further stability for both D_2O

and N_2H_4 adsorbates. No other interactions or reactions between the two adsorbates, other than this low-temperature proton exchange, were identified in our experiments.

We end with a brief discussion of the implications of the chemistry described here to the possible uses of hydrazine in relevant catalysis or materials applications. As mentioned in the introduction, hydrazines have been suggested as possible nitridation agents [13; 28; 55; 56], but the fact that N–H bond scission steps dominate over the activation of the N–N bond on copper surfaces, at least at high coverages, suggests that this type of nitridation may not be particularly effective. On the other hand, the ease with which hydrazine dehydrogenates and becomes oxidized to diazene and to molecular nitrogen makes it a good and clean source of hydrogen, both as $\text{H}(\text{ads})$ on the surface and as H_2 (for fuel applications [17; 23]), and also a potential reducing agent. In ALD applications in particular [29; 33; 57; 58], hydrazine is expected to be a much more effective co-reactant than ammonia for the reduction of copper precursors to grow thin copper films. Given the difficulty of activating molecular hydrogen on copper surfaces [59; 60], hydrazine may also be a good substitute for H_2 in ALD for film growth on Cu substrates.

The role of hydrazine in the ALD process recently proposed by the Winter group [30], which also requires formic acid and a viable copper metalorganic precursor, may be more complex, but may still involve atomic hydrogen transfer steps: the fast H-D exchange between hydrazine and D_2O on $\text{Cu}(110)$ seen here at cryogenic temperatures attests to the ease with which such reactions are expected to take place. Furthermore, given the difficulty shown here for hydrazine to form $\text{NH}_x(\text{ads})$ surface moieties on Cu surfaces, it is not very likely that such intermediates participate in the ALD chemistry [31]; it is more probable for $\text{N}_2\text{H}_y(\text{ads})$ intermediates to be

involved instead. One possibility is for the copper formate resulting from the conversion of Cu precursors with formic acid to be reduced by the hydrazine according to the following stoichiometries:

In this proposed mechanism, hydrazine acts as the sole reducing agent of the copper ions, without additional redox chemistry from either the formate ligands or formic acid, and molecular nitrogen rather than ammonia is made as the byproduct. It is still possible that some hydrazine is reduced by formic acid as well, via the stoichiometry in Equation (3) as suggested before [31]:

This idea seems feasible given that ammonia is also made during the thermal decomposition of hydrazine on Cu(110). Nevertheless, the surface intermediates in such case are still expected to be $\text{N}_2\text{H}_y(\text{ads})$, not $\text{NH}_x(\text{ads})$, species, and the actual surface moieties promoting the reduction of hydrazine to be a formate (perhaps coordinated to the copper ion, as indicated in Equations (2) and (3)), not formic acid, which only binds weakly to copper [42]. These ideas complicate the simple mechanism initially put forward to explain the Cu precursor/formic acid/hydrazine ALD process [30; 31], but a more complete picture of the surface chemistry involved will require still further experimental and theoretical work.

5. Conclusions

Survey temperature programmed desorption (TPD) experiments with hydrazine adsorbed on a Cu(110) single-crystal surface at cryogenic temperatures identified the evolution of molecular hydrazine at 170 K as well as the production of molecular nitrogen, and ammonia at 350 and 360 and 300 - 700 K respectively. In addition, small amounts of diazene and $\text{NH}_2\cdot$ radicals, at 250 - 400 and 300 - 700 K respectively, were also detected. Interestingly, no significant H_2 production was observed. A set of experiments as a function of initial hydrazine dose showed a clear transition from the predominance of desorption of NH_3 and $\text{NH}_2\cdot$ at low coverages to a partial switch to N_2 formation and the suppression of the radical ejection for exposures of 4 L and above. An additional low (320 K) N_2 peak also develops in the TPD for doses above about 15 L. Adsorption of hydrazine on Cu(110) at 300 K leads to the stabilization of surface intermediates, which now yield gas-phase products only above 400 K: H_2 , N_2 and NH_3 are all seen at 430 and 470 K, and diazene at slightly lower temperatures.

Exposure of the Cu(110) to oxygen prior to the hydrazine uptake helps stabilize the adsorption of the latter, as indicated by the delay of some of the molecular N_2H_4 desorption to temperatures of up to 500 K. Also, the new low-temperature N_2 TPD peak, only seen after higher doses on clean Cu(110), is detected with 5.0 L N_2H_4 in the presence of the surface oxygen, possibly because that oxygen offers further crowding of the surface, inducing a change in adsorption geometry akin to that resulting from further hydrazine uptake. Coadsorption of N_2H_4 and D_2O on either clean or oxygen-pretreated Cu(110) surfaces results in the production of NH_2D in TPD experiments. The

desorption kinetics of that product is the same as on the clean metal, and all water desorbs below 200 K, in the same fashion as in D₂O/Cu(110), which means that the hydrazine and water must undergo isotope scrambling at cryogenic temperatures. Once water desorbs, the remaining thermal behavior of the coadsorbed system resembles that seen without any water.

XPS data provide further support for the surface chemistry established for hydrazine on Cu(110) from analysis of the TPD data. For one, the major intensity change in the N 1s XPS signals occurs in the same temperature range where the main TPD products, N₂ and NH₃, are seen, namely, around 350 K on clean Cu(110) and between 300 and 350 K in the O/Cu(110) case. In addition, though, two more pieces of information were extracted from the XPS data: (1) the N 1s XPS peak shifts to higher binding energies with increasing heating temperature, indicating the prevalence of dehydrogenation steps over N–N bond scission and the formation of N₂H_y(ads) intermediates, including diazene (N₂H₂) rather than NH_x(ads) moieties; and (2) on the oxygen pretreated surfaces, the O 1s XPS peak also shifts to higher binding energies with increasing temperature, as expected from the formation of surface OH groups via hydrogen-transfer steps. It appears that adsorbed atomic oxygen may aid in the dehydrogenation of hydrazine on Cu(110).

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Figure Captions

Figure 1. Survey temperature programmed desorption (TPD) data from 4.0 L of hydrazine adsorbed on clean Cu(110) at 140 K. Shown are traces for (from bottom to top) 2, 12, 14, 18, 29, 32, 16, 17, and 28 amu. The main desorbing species detected in these experiments are molecular nitrogen (14 and 28 amu), ammonia (16 and 17 amu), and molecular hydrazine (32 amu), but small amounts of diazene (29 amu) and $\text{NH}_2\cdot$ radicals (16 amu) are seen as well.

Figure 2. TPD traces for (from left to right) N_2H_4 (32 amu), N_2 (28 amu), NH_3 (17 amu) and $\text{NH}_2\cdot$ (16 amu, corrected for the contribution from ammonia) as a function of initial exposure from hydrazine adsorbed on clean Cu(110). NH_3 and $\text{NH}_2\cdot$ desorption dominates at exposures below 4 L, but N_2 becomes the preferred product at higher doses.

Figure 3. Survey TPD from 10 L of hydrazine dosed on clean Cu(110) at 300 K. Shown are data for (from bottom to top): 2, 14, 16, 17, 28, 29, and 32 amu. Desorption of H_2 (2 amu), $\text{NH}_2\cdot$ (16 amu), NH_3 (16 and 17 amu), and N_2 (14 and 28 amu) are all seen in two stages between about 400 and 500 K, and diazene (29 amu) is observed at slightly lower temperatures.

Figure 4. TPD data from 5.0 L of hydrazine adsorbed on clean (left panel), perdeutero-water predosed (0.1 L D₂O, second panel), oxygen predosed (0.1 L O₂, third panel), and perdeutero-water plus oxygen predosed (0.1 L O₂, then 0.5 L D₂O, last panel) at 140 K. Traces are shown in each case for (from bottom to top): 2, 17, 18, 20, 32, and 28 amu.

Figure 5. D₂O (20 amu) TPD results from D₂O adsorbed on clean (left panel) and oxygen-predosed (right) Cu(110). Left: TPD traces versus D₂O initial exposure (1.0, 2.0, 3.0, and 6.0 L, starting from the second trace from the bottom up). The bottom spectrum, which corresponds to 5.0 L N₂H₄ dosed after 0.5 L of D₂O, is provided for comparison. Right: Top: TPD traces from 2.0 L D₂O adsorbed on a Cu(110) surface predosed with 0.1 L O₂; Bottom: data obtained after the sequential dosing of 0.5 L O₂, 0.5 L D₂O, and 5.0 L of N₂H₄.

Figure 6. X-ray photoelectron spectra (XPS) from 5.0 L of N₂H₄ dosed at 140 K on clean (left panel) and oxygen-pretreated (two right panels) Cu(110). The first two panels are for the N 1s XPS peak, the last corresponds to the O 1s XPS signal. Traces are shown in each panel as a function of heating temperature. Two left panels (from top to bottom): 150, 200, 250, 300, 350, and 400 K, and blank surface (clean and oxygen predosed, respectively, taken before N₂H₄ dosing). Right panel (from top to bottom): Blank (oxygen predosed) surface, and after dosing the N₂H₄ and heating to 150, 200, 250, 300, 350, and 400 K. Oxygen pretreatment: 1×10^{-6} Torr of O₂ at 500 K for 10 min.

Figure 7. Summary of the XPS data shown in Figure 6 in the form of peak areas (left panel) and peak positions (binding energies, BEs, right) versus heating temperature. Left: Cu 2p_{3/2} (solid dark blue and open dark red squares, raw spectra not shown), N 1s (solid light blue and open light red circles), and O 1s (solid purple diamonds) XPS signal intensities, corrected for differences in spectrometer sensitivities and scaled to add up to approximately one monolayer (1 ML = 1 atom/molecule per exposed Cu atom). The solid symbols and dashed lines correspond to the clean Cu(110), the open symbols and solid lines to the oxygen pre-exposed surfaces. Right: N 1s XPS peak positions versus temperature (same symbol, line and color convention as on the left).

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6

Figure 7

Graphical Abstract