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Adsorption of azomethane on Cu(1 1 0) and Cu(1 1 1) surfaces

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Abstract

The interactions of azomethane on Cu(1 1 0) and Cu(1 1 1) have been investigated with XPS and HREELS under various exposure and surface temperature conditions. It is shown that with substrate at 90 K, the chemisorbed molecule is likely in *cis*-form on the Cu(1 1 0) surface, but retains the *trans*-form on Cu(1 1 1). The adsorbed azomethane desorbs molecularly when the Cu(1 1 1) surface is annealed to 190 K. In contrast, the interaction between $CH_3N_2CH_3$ and Cu(1 1 0) weakens the strength of N=N bond leading to the formation of NCH_2 and NCH_3 above 190 K. In addition, some adsorbed molecules undergo C–N cleavage accompanied with dehydrogenation reaction to form CH_2. Characteristic vibrational frequencies for the observed radicals on Cu(1 1 0) are determined. From XPS data, the binding energies of C(1s) and N(1s) of azomethane are found to be near 286.3 and 401.4 eV, respectively. These values shift to 285.4 and 400.3 eV when azomethane dissociates to form NCH_3 and NCH_2. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Azomethane; Copper surface; Hydrocarbon radical; XPS; HREELS

1. Introduction

Hydrocarbon radicals play important roles in heterogeneous catalysis and materials processing. Methyl radical is an essential hydrocarbon species and there are extensive interests in its chemistry on transition metal surfaces [1–12]. The interaction of methyl radical with Cu(1 1 1) has been studied in our previous work [13,14]. Pyrolysis of azomethane molecules ($CH_3N_2CH_3$) above 1100 K is frequently used as a means to generate methyl radicals [15]. Accordingly, there have been some studies of azomethane interactions with various surfaces, aiming at heterogeneously producing CH_3 [16–23]. It appears, however, that in all studies on transition metals, the molecule predominantly breaks at N–N bond but not at N–C bond. It was reported that C–N bond cleavage could be induced by pretreating a surface with oxygen atoms such as the oxygen-covered Ru(1 1 1) [23]. Excitation of electronic states could also increase the possibility of C–N bond scission, such as the electron-induced decomposition of azomethane on Ag(1 1 1) [21], and the photolysis of azomethane on Pd(1 1 1) [20].

An important consideration for understanding the catalytic reaction is how the molecule initially bonds to the surface. In the study of azomethane on Pt(1 1 1), Jentz et al. [22] proposed that the molecule was bonded to the surface via the nitrogen lone pairs. The N–N

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scission of adsorbed azomethane was suggested to proceed through isomerization to *cis*-azomethane upon adsorption at 84 K, and then tautomerization to form formaldehyde methylhydrazone (CH_3-$NHNCH_2$) when annealed to 200 K. Similarly, it was reported by Bol et al. [16] that azomethane isomerized to the *cis*-isomer upon adsorption via the nitrogen lone pairs on Mo(1 1 0) at 100 K.

Herein, we report the study on the interaction of azomethane on Cu(1 1 0) at various temperatures, and the results are compared with our previous work on Cu(1 1 1). It is found that the chemistry was drastically different between these two surfaces.

2. Experimental

The experiments were carried out in a UHV system equipped with XPS, AES, TDS, LEED and HREELS. Details of the apparatus, the routine cleaning procedure of Cu surface, and the synthesis method of azomethane have been described previously [13,14]. For present HREELS measurements, the incident electron energy was fixed at 4.68 eV with an incident angle of 44° from the surface normal. A spectral resolution of 3.5 meV (FWHM of elastic peak) was used. Most of the loss signals were collected in the specular direction. For gaseous dosing, an effusive nozzle source directly facing the sample at a distance of 3.5 cm was utilized. In low temperature studies, azomethane gas at 300 K was introduced through the nozzle onto the clean Cu surface held at 90 K. In the annealing measurements, the sample was warmed to various temperatures and cooled down again to 90 K for spectral analysis.

3. Results and discussion

The XPS data for azomethane adsorbed on Cu(1 1 0) at 90 K with various coverages are shown in Fig. 1. The surface coverage (θ) as a function of gaseous exposure can be estimated from the attenuation of Cu($2P_{3/2}$) signal at 932.4 eV. At a submonolayer coverage ($\theta < 1$), the C(1s) binding energy (BE) is found at 286.0 eV which shifts slightly to 286.3 eV at multilayer coverages. In N(1s) region, only one peak is detected at 401.4 eV. The C(1s) and N(1s) spectral widths (FWHM) are 1.8 and 2.0 eV, respectively, and independent of surface coverage. Comparing these values with the FWHM (1.7 eV) of Cu($2P_{3/2}$), it is evident that there exists only one dominant species on Cu(1 1 0) after azomethane exposure at 90 K. Furthermore, the intensity ratio (integrated areas normalized with ionization cross sections) of C(1s):N(1s) remains essentially unity for all exposures. Therefore, it is concluded that azomethane adsorbs on Cu(1 1 0) in molecular form at this temperature similar to the $CH_3N_2CH_3$/Ag(1 1 1) system [21].

When the temperature of Cu(1 1 0) with a multilayer coverage is raised to 200 K and cooled back to 90 K, we find the XPS signals are greatly reduced corresponding to a submonolyer coverage (Fig. 1d and e). The BE of C(1s) is located at 285.5 eV and that of N(1s) at 400.3 eV. The C:N intensity ratio increases by almost a factor of 2. The C(1s) spectrum is broadened substantially and in fact exhibits a shoulder at 284.7 eV. The result indicates that physisorbed azomethane (above a monolayer) desorbs below 200 K, and some chemisorbed molecules ($\theta \leqq 1$) in direct contact with Cu(1 1 0) are decomposed to form NCH_x compounds as well as hydrocarbon species such as CH_2 due to the temperature effect.

Fig. 2a depicts the typical HREELS spectrum for $\theta < 1$ on Cu(1 1 0) at 90 K. The characteristic vibrational bands at 596, 927, 1362, 1427 and 1516 cm^{-1} can be assigned to CNN bend (δ-CNN), CH_3 rock (δ-CH_3), CH_3 s-deformation (δ_s-CH_3), CH_3 as-deformation (δ_{as}-CH_3), and N=N stretch modes, respectively. In the high frequency regime, the C–H stretch mode involving CH_3 group of the molecule appears at 2967 cm^{-1}. The signal near 2000 cm^{-1} is due to a small amount of CO coadsortion at 90 K. As the surface coverage is increased beyond a monolayer, we observe drastic changes in relative peak intensities of vibrational signals. At a multilayer coverage, the most prominent features are at 1104 (ρ-CH_3), 1427 (δ-CH_3) and 2976 cm^{-1} (CH_3 stretch), whereas the main peaks as 596, 926, 1362 and 1514 cm^{-1} for $\theta \leqq 1$ are greatly reduced in intensity. In fact, the HREELS spectrum for $\theta > 1$ on Cu(1 1 0) at 90 K is rather similar to that for $\theta \leqq 1$ on Cu(1 1 1) as displayed in Fig. 2b. On Cu(1 1 1), the vibrational spectrum does not vary significantly as a function of θ. By comparing the HREELS data with the IR spectra of condensed

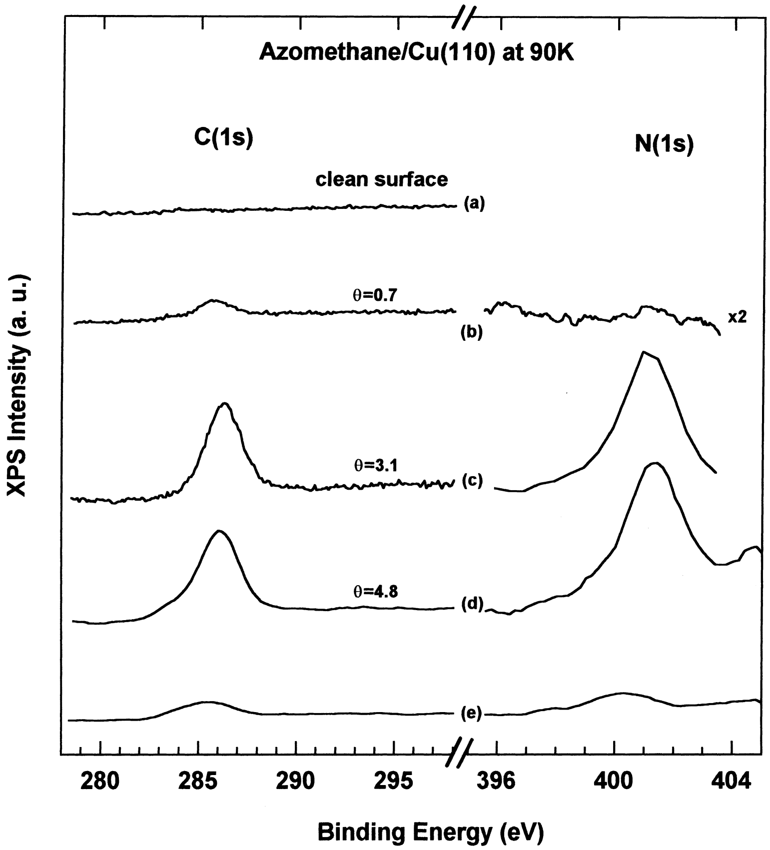

Fig. 1. C(1s) and N(1s) XPS spectra for $CH_3N_2CH_3$/Cu(1 1 0) at 90 K and various coverages: (a) clean surface, (b) $\theta = 0.7$, (c) $\theta = 3.1$, (d) $\theta = 4.8$, and (e) sample (d) annealed to 200 K, resulted in $\theta < 1$.

phase *cis*- and *trans*-azomethane [24,25], we can conclude that in the multilayer coverage on both Cu(1 1 0) and Cu(1 1 1) as well as in the submonolyer coverage on Cu(1 1 1), the adsorbed molecules remain in the *trans*-form like in the gas phase. In contrast, the molecular geometry is likely in the *cis*-form on Cu(1 1 0) at $\theta \leqq 1$.

The frequency of N=N stretching above 1500 cm^{-1} indicates sp^2 hybridization for the N atoms, so that the C–N=N–C skeleton is planar. By considering the surface as flat and featureless, the submonolayer *trans*-azomethane on surface has C_2 and C_s two possible adsorption geometries while the *cis*-azomethane has adsorption geometry of C_{2v} or C_s symmetry [22]. Comparing the solid phase IR spectra [25] with our HREELS data (Fig. 2(a)) for $CH_3N_2CH_3$ on Cu(1 1 0), it obviously has two differences. First, in v (C–H) frequency region, the infrared spectra of polycrystalline azomethane have two strong absorption peaks at 2911 and 2975 cm^{-1} whereas the HREELS exhibits only one dominant peak centered at 2967 cm^{-1}. Secondly, in Fig. 2(a), peaks at 596, 927 and 1516 cm^{-1} have relatively high intensities while these peaks are absent in IR spectra. This suggests, according to the dipole selection rule that the molecular symmetry is altered when the molecule is in direct contact with the Cu(1 1 0) surface. In a prior study on azomethane/Pt(1 1 1), Jentz et al. [22] suggested the absence of 2911 cm^{-1} peak and the strong intensity at 1510 cm^{-1} as indications that the molecule was adsorbed in *cis*-form. From this point of view, the differences we have mentioned above probably imply that azomethane also undergo isomerization and adsorb in *cis*-form on Cu(1 1 0). Table 1

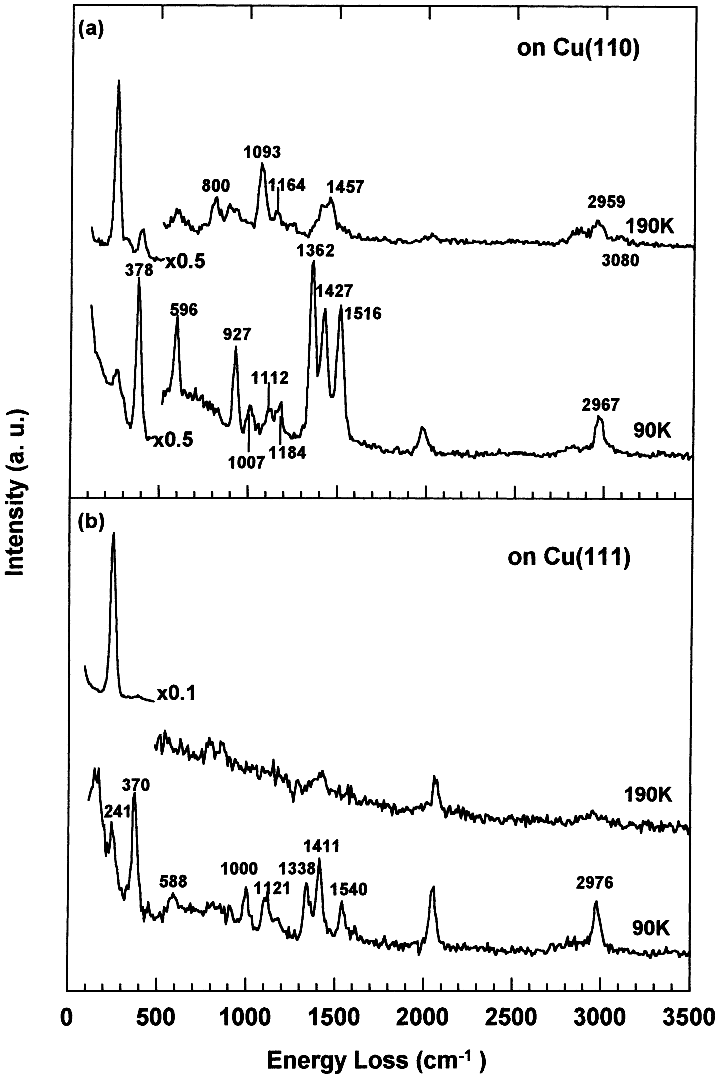

Fig. 2. The HREELS spectra for $CH_3N_2CH_3$ on (a) Cu(1 1 0) and (b) Cu(1 1 1), initial exposures at 90 K with $\theta < 1$, and then annealed to 190 K.

summarizes the observed frequencies, mode assignments and the comparison with solid *cis*- and *trans*-azomethane.

When the temperature of Cu(1 1 0) with $\theta \leqq 1$ is raised to 190 K, some molecules are desorbed, and some are decomposed into NCH_3(ads), NCH_2(ads) and CH_2(ads). Practically, all characteristic vibrational features of molecular azomethane disappear. Apparently breaking of both N=N and C–N bonds can occur at this temperature. The formation of NCH_3 species can be identified from the strong signals at 1093 cm^{-1} (ν C–N) and 2959 cm^{-1} (ν-CH_3) as depicted also in Fig. 2a. The peaks near 800 cm^{-1} (ρ-CH_2) and 3080 cm^{-1} (ν-CH_2) indicate the presence of NCH_2. The emerging of signals near 1164 cm^{-1} (ω-CH_2) and 1353 cm^{-1} (δ-CH_2, scissors) suggests the production of CH_2. These signals become clearer at higher substrate temperatures as NCH_2 and NCH_3 are further decomposed to form CH_2(ads). The HREELS data are consistent with XPS result which

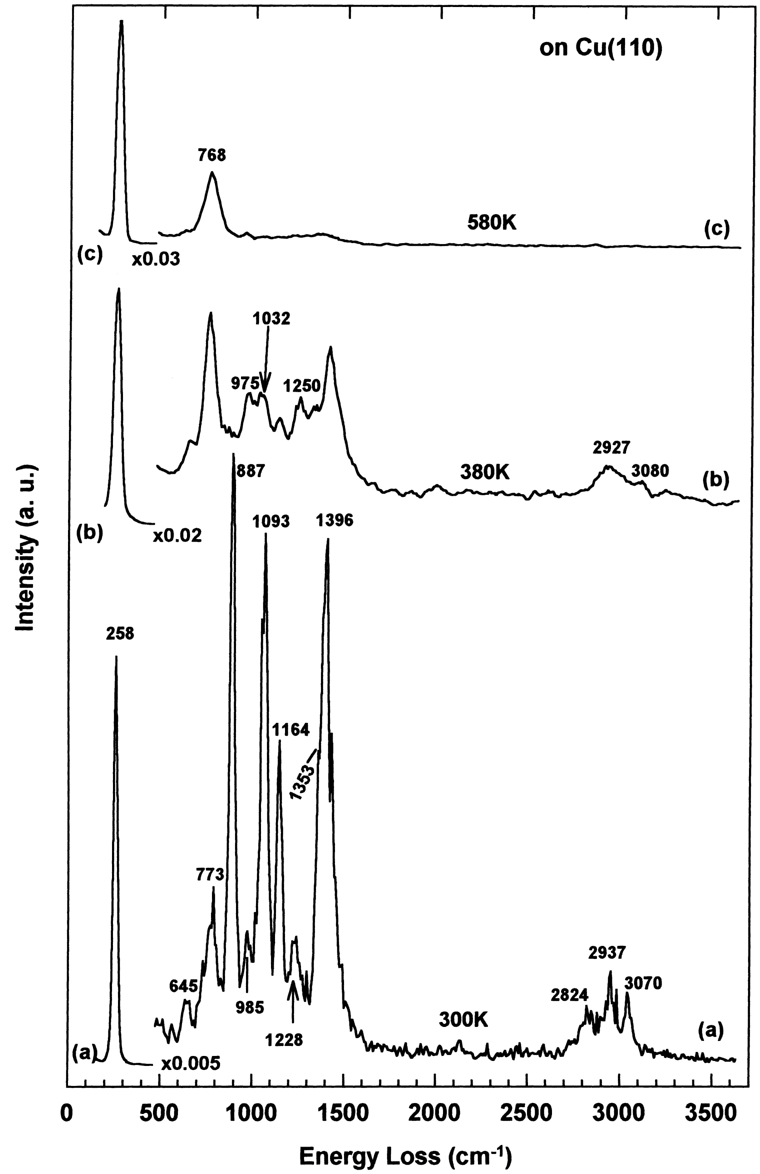

Fig. 3. The HREELS spectra for $CH_3N_2CH_3$ on Cu(1 1 0) at 300 K for about 40 l exposure (a), and then annealed to 380 K (b) and 580 K (c).

exhibits a shoulder at 284.7 eV. From our previous work [14], CH_2(ads) on Cu(1 1 1) shows the C(1s) BE at this value. In drastic contrast to azomethane on Cu(1 1 0), the molecule on Cu(1 1 1) at 90 K simply desorbs above 190 K (Fig. 2b). No evidence of molecular decomposition is observed on this surface in agreement with a prior study [26].

Fig. 3a displays the HREELS spectrum for Cu(1 1 0) at 300 K exposed to azomethane for about 40 Langmuir. The main peaks are at 645, 773, 887, 985, 1093, 1164, 1228, 1396, 2824, 2937 and 3070 cm^{-1}. The relative intensities of these signals change somewhat as a function of gaseous exposure. Based on previous works [13,14,20,22,23,27], we can

Table 1
$CH_3N_2CH_3$/Cu(1 1 1) and $CH_3N_2CH_3$/Cu(1 1 0) observed vibrational frequencies (cm^{-1}), mode assignments and comparison with solid phase azomethane

$CH_3N_2CH_3$/Cu(1 1 0) (present work) monolayer (90 K)		$CH_3N_2CH_3$/Cu(1 1 1) (present work) monolayer (90 K)	$CH_3N_2CH_3$ (solid phase, 103 K) *trans*-azomethane[a]	$CH_3N_2CH_3$ (solid phase, 77 K) *cis*-azomethane[b]
202	Cu surf. phonon	–	–	–
378	CNN bend (δ-CNN)	370	362	390
596	CNN bend (δ-CNN)	588	584	630
927	CH_3 rock (δ-CH_3)	–	916	866
1007	CH_3 rock (ω-CH_3)	1000	1001, 1026	954
1112	CH_3 rock (ρ-CH_3)	1121	1112	1170
1184	CN stretch (ν-CN)	–	1176	1178
1362	CH_3 deformation (δ_s-CH_3)	1338	1386	1361, 1369
1427	CH_3 deformation (δ_{as}-CH_3)	1411	1450	1472, 1466
1516	N=N stretch (ν-NN)	1540	1574	1556
2967	CH_3 stretch (ν-CH)	2976	2911, 2975	2986, 3008

[a] [25].
[b] [24].

assign 645, 985, 1164, 1353 and 2824 cm^{-1} peaks to CH_2(ads). The peaks at 773, 1093 and 3070 cm^{-1} belong to NCH_2(ads), and those at 887, 1093, 1164, 1396 and 2937 cm^{-1} to NCH_3(ads). Thus, at 300 K, all these three species can coexist on Cu(1 1 0). When the substrate temperature is raised to 380 K (Fig. 3b), the signal intensities attributed to NCH_2 and NCH_3 drop dramatically whereas those associated with CH_2 remain relatively strong. The most drastic effect, however, is the rise of a broad band at 768 cm^{-1} due to CH formation. Clearly NCH_2 and NCH_3 can desorb and/or decompose to yield CH_x(ads) at this temperature. At 580 K (Fig. 3c), the only species that is still present on Cu(1 1 0) is CH(ads).

In Summary, we have observed by XPS and HREELS that for azomethane chemisorption, the surface reactivity on Cu(1 1 0) is much higher than on Cu(1 1 1). The molecule in direct contact with Cu(1 1 0) at 90 K can be isomerized or distorted. The N=N bond is weakened due to adsorbate-surface interaction and can be broken at 190 K to form NCH_2 and NCH_3. In addition, C–N bond cleavage and dehydrogenation can take place to produce CH_2. In contrast, the molecule adsorbs on Cu(1 1 1) in gaseous geometry at 90 K and simply desorbs near 190 K. The study demonstrates that azomethane exposure on Cu(1 1 0) at 300 K is an effective method for generating NCH_2 and NCH_3 species. They can dissociate further above 380 K to form CH species which can eventually be desorbed and decomposed to residual carbon on the surface above 700 K.

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