Thermal Chemistry of Adsorbed Molecules Containing Azido and Cyano Groups on a Copper Surface

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In the organometallic chemistry, the imido complexes are an interesting species because of their manifold reactivities. There are two forms of imido, M=N-R (nucleophilic) and M≡N-R (elctrophilic) form.[1] The decomposition of metal azido complexes are known to result in formation of corresponding metal nitride(M≡N) or imido complexes.[2] We attempt to use the azidotrimethylsilane ($(CH_3)_3Si\text{-}N_3$; $TMSN_3$) as precursors to produce imido species (TMSN=Cu) followed by N_2 extrusion on Cu(111). The process was explored by combining temperature-programmed desorption (TPD), reflection absorption infrared spectroscopy (RAIRS), and X-ray photoemission spectroscopy (XPS) techniques. In addition, density functional theory (DFT) calculations were conducted to obtain optimized geometries of the various surface intermediates. The computed IR spectra facilitated the vibrational mode assignments.

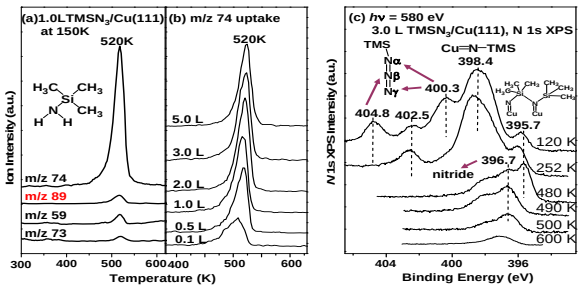

Fig. 1: TPD spectra resulting from (a) azidotrimethyl-silane adsorption on Cu(111), (b) various coverage for m/z 74 and (c) temperature-dependant N 1s XPS show formation of imido species and relative hydrogenation product (trimethylsilanamine).

TPD spectra show that TMSN=Cu was hydrogenated to $TMSNH_2$ amine around 520 K, as shown in Fig. 1a. We propose that the hydrogen source is adsorbed methyl groups, invoking the cleavage of the Si-C bond. The uptake of TMSNH yields as a function of exposure exhibits a saturation behavior, instead of passing through a maximum, asshown in Fig. 1b. Moreover, temperature dependent XPS reveal that TMSN=Cu result from thermodecomposition of TMSN3 below 252K.

As TMS group is separated from nitrogen by a methylene moiety, TPD specta implys evolution of $TMSCH_2N_3$ into TMSCN at 280K (as comparison of Figs. 1a and 1b). Furthermore, XPS ans RAIRs suggest TMSCN is as result of C-N_α bond cleavage followed by α,α H- elimination of $TMSCH_2$-Cu and metathesis.

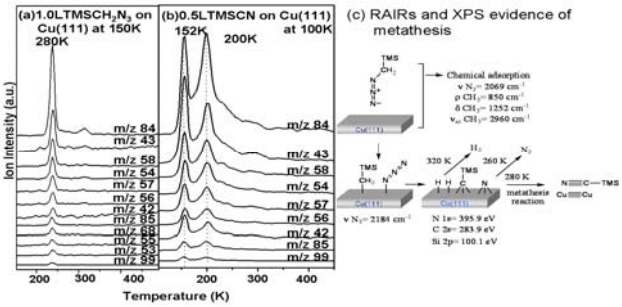

Fig. 2: (a) TPD spectra of 1.0L TMSCH2N3 on Cu(111) at 150K and (b)0.5L TMSCN on Cu(111). Combined information from RAIRS and XPS implies metathesis reaction occurs.

Investigation of TMSCN by RAIRs and DFT calculation was shown in Fig. 3. Absence of the band at 2186 cm^{-1} being assignmented as stretching of C≡N bond (νC≡N) of TMSCN (suggested by DFT calculated spectum) at 280K and the growth of the band at 2061 cm^{-1} being assignmented as stretching of N≡C bond (νN≡C) of TMSNC (suggested by DFT calculated spectum) at 210K reveal isomerization of TMSCN is switched on at ~210K and the product, TMSNC, desorbs at 410K.

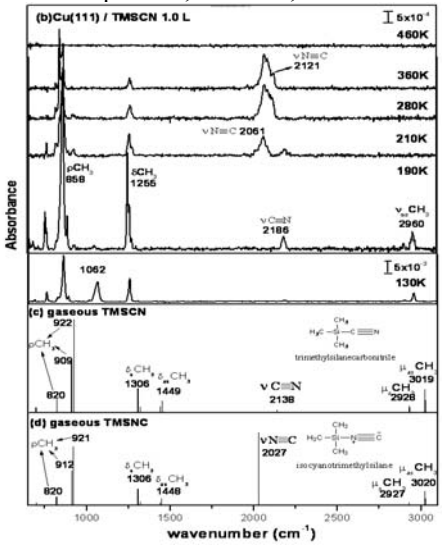

Fig. 3: Temperature dependant RAIRS of TMSCN reveal that TMSCN isomerizes into TMSNC at 210K.

References

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[2] R. A. Eikey and M. M. Abu-Omar, Coord. Chem. Rev. **243**, 83 (2003).