

Chapter 3

NH₃ adsorption on Cu₂O (111) surfaces

3.1 Introduction

As discussed in the previous chapter, Lewis bases such as ammonia and pyridine are common probe molecules in catalysis to characterize acidic properties of oxide surfaces [1]. The relationship between acidic properties and observed chemistry is often investigated to give insight into the nature of oxide reactivity [1]. The nature of acidic sites on oxide surfaces can be described in Lewis and Brønsted terms. For clean metal oxide surfaces (no surface protons), the properties are principally described in terms of Lewis acidity. On metal oxides, coordinatively unsaturated metal cations are generally thought to be Lewis acid sites since the electron-deficient metal cations exhibit acidic, electron-acceptor character [2,3].

The non-polar Cu₂O (111) surface can be prepared in a stoichiometric, (1×1) form (Figure 1a) or a non-stoichiometric, ($\sqrt{3}\times\sqrt{3}$)R30° form (Figure 1b) that is associated with the loss of one-third of the outer-layer of oxygen anions [4]. The surface oxygen anions in the outer atomic layer have a coordination of three on the (111) surfaces. The bulk coordination of the Cu⁺ cation is two, and the exposed surface cations are singly coordinate. Therefore, the adsorption behavior on cation sites associated with anion vacancies can be tested with changes in local geometry arising from oxygen vacancies but no apparent change in the coordination of the surface cations relative to that of the stoichiometric surface.

The adsorption and dissociation of propene at low temperature (100 K) and low pressure ($<10^{-6}$ Torr) has been investigated previously on Cu_2O (111) surfaces [5]. Propene dissociates to a hydrogen and an allyl on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ Cu_2O (111) surface at low temperature [5]. Since the methyl hydrogens are the most acidic for gas phase propene, the dissociation to allyl has been viewed in acid/base terms as the dissociation of a weak Brønsted acid to a proton and an allyl anion. Only the oxygen-deficient, $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ Cu_2O (111) surface (Figure 1b) has been found to activate the dissociative acid/base reaction of propene to surface allyl at low temperature and pressure. In previous TPD experiments, the recombination of surface allyl and hydrogen for propene desorption has been clearly associated with the presence of the oxygen vacancies on this surface [5]. However, this observed dissociation behavior of propene is not well understood. In particular, the relationship between local surface properties and the acid/base properties of the site pairs remains undefined.

In the present work, the chemisorption of a standard basic probe molecule, ammonia, has been examined over Cu_2O (111). The first aim of the study is to understand the details of the interaction of ammonia at specific, well-defined sites on an oxide surface. The second goal of the study is to use this probe molecule as a standard characterization of the acidity of different cation sites with the goal of determining whether a simple acid/base description is applicable to the previous results for propene dissociation [5].

3.2 Experimental

For TDS experiments, all surfaces were exposed to NH₃ at 120 K and heated to 650 K using a linear temperature ramp of 2 K/sec. During TDS experiments, the background pressure was less than 2×10^{-10} Torr between doses. For UPS experiments, all surfaces were also exposed to NH₃ at 120 K.

3.3 Results

3.3.1 Thermal Desorption Spectroscopy

TDS of NH₃ can be thought of as a way to provide a measure of the strength of the Lewis acidity of cations associated with specific sites. Variations in NH₃ adsorption were examined by TDS for both preparations described above. All desorption features are thought to be first-order and originate from a molecular NH₃ adsorbate. Only NH₃ was observed by thermal desorption following NH₃ adsorption. Desorption of H₂, H₂O, and N₂ was checked for but not observed. The lack of reaction products suggests no dissociation of NH₃. A second-order Redhead analysis of the TDS data shows no linearity suggestive of second-order behavior that might indicate a NH₃ recombination process [6].

3.3.1.1 Nearly-stoichiometric surface

The coverage dependence of the NH₃ desorption traces from a clean, nearly-stoichiometric surface is illustrated in Figure 3.1. At the lowest NH₃ exposure investigated, 0.02 L (1 L = 10^{-6} Torr-sec), one broad NH₃ desorption feature is observed over a range of temperatures from 250 to 500 K and is designated as the α_1 state. Increasing the NH₃ exposure to 0.05 L, a new NH₃ desorption feature is observed at 240

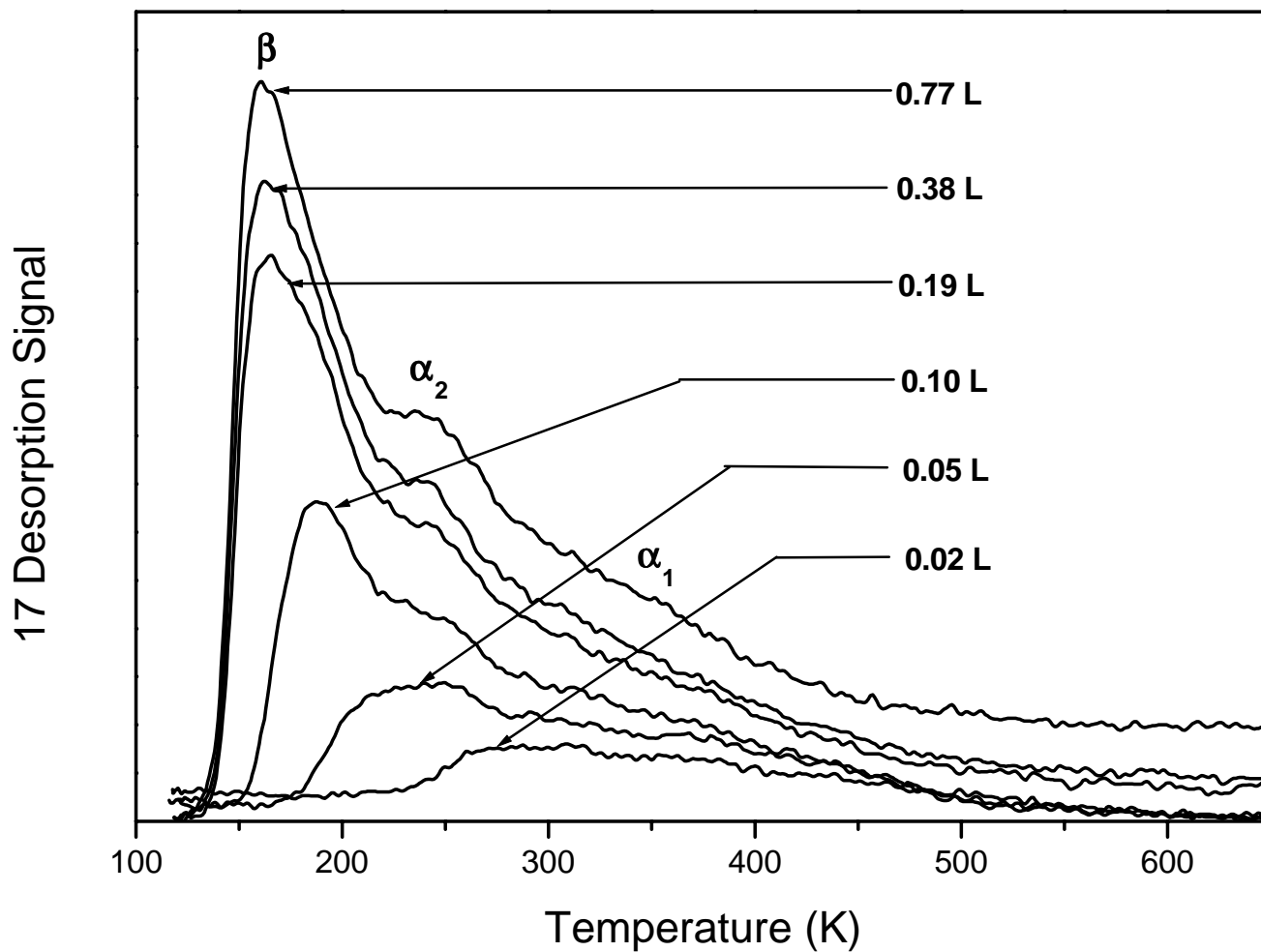


Figure 3.1 Ammonia TDS traces following adsorption at exposures of 0.02 L to 0.77 L at 120 K on a nearly-stoichiometric Cu_2O (111) surface.

K and is specified as the α_2 state. At an NH_3 exposure of 0.1 L, another new NH_3 desorption feature appears at 190 K. This feature at 190 K shifts down in temperature to 160 K with increasing coverage and is referred to as the β state. Assuming a normal pre-exponential of 10^{13} s^{-1} , a range of 9.8-11.7 kcal/mol for the first-order activation energy for desorption can be calculated for the low-temperature (160-190 K) TDS feature, 14.8 kcal/mol for the 240 K TDS feature, and a range of 15.5-31.6 kcal/mol for the broad 250-500 K feature using the Redhead equation [6]. No attempt was made to independently determine the pre-exponential via the method of heating rate variation. TDS spectra are shown for only small NH_3 exposures, 0.02-0.8 L, because NH_3 desorption signals from the sample support hardware are apparent for larger exposures. NH_3 uptake saturates at an exposure of 0.4 L (see UPS results below), and intensity differences for larger exposures are due to variations in the background contributions.

3.3.1.2 Oxygen-deficient ($\sqrt{3}\times\sqrt{3}$)R30° surface

The coverage dependence of the NH_3 desorption traces on the oxygen-deficient ($\sqrt{3}\times\sqrt{3}$)R30° surface are essentially indistinguishable from the NH_3 desorption behavior seen on the nearly-stoichiometric surface. Therefore, NH_3 desorption behavior in TDS shown in Figure 3.1 is representative of both surfaces. No significant modification of the desorption traces is seen due to the removal of one-third of a layer of oxygen anions.

3.3.2 He I UPS measurements

3.3.2.1 Changes in surface electronic properties with NH_3 adsorption

He I UPS was used to study changes in surface electronic properties upon adsorption. Changes in work function, band bending, and surface dipole following NH_3 adsorption on the nearly-stoichiometric and $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surfaces are shown in Figure 3.2 as a function of dose for NH_3 adsorption at 120 K. Changes in work function were measured by shifts in the vacuum level cutoff of the He I spectra as seen in Chapter 2. For a semiconductor, these changes in the work function ($\Delta\phi$) include contributions due to band bending ($-e\Delta V_s$) and changes in the surface dipole ($\Delta\chi$) according to the relationship, $\Delta\phi = \Delta\chi - e\Delta V_s$ [7-8]. Band bending changes were determined from the shifts in the low-binding energy edge of the substrate features near the valence band maximum, and the change in surface dipole was calculated from the work function and band bending changes as seen in Chapter 2. The largest contribution to changes in the work function is accounted for by the surface dipole.

Figure 3.2 shows decreases in the work function, downward band bending, and decreases in the surface dipole for the nearly-stoichiometric and $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surfaces. The surface dipole decreases with increasing exposures up to 0.4 L for all surfaces (shown in Figure 3.2), and indicates that saturation of the surface by NH_3 is achieved by an 0.4 L exposure. A decrease in the surface dipole upon NH_3 adsorption indicates that charge is transferred from the NH_3 molecules to the surface, suggesting the NH_3 molecules bind to the surface via the nitrogen lone pair. The decrease in surface dipole of the nearly-stoichiometric surface is 1.2 eV at saturation. For the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface, the change in dipole is slightly larger, decreasing by 1.4 eV at saturation. From the variation in $-e\Delta V_s$, it is apparent that the bands bend down with increasing NH_3 exposures for both surfaces until NH_3 saturates the surface at 0.4 L (shown in Figure 3.2).

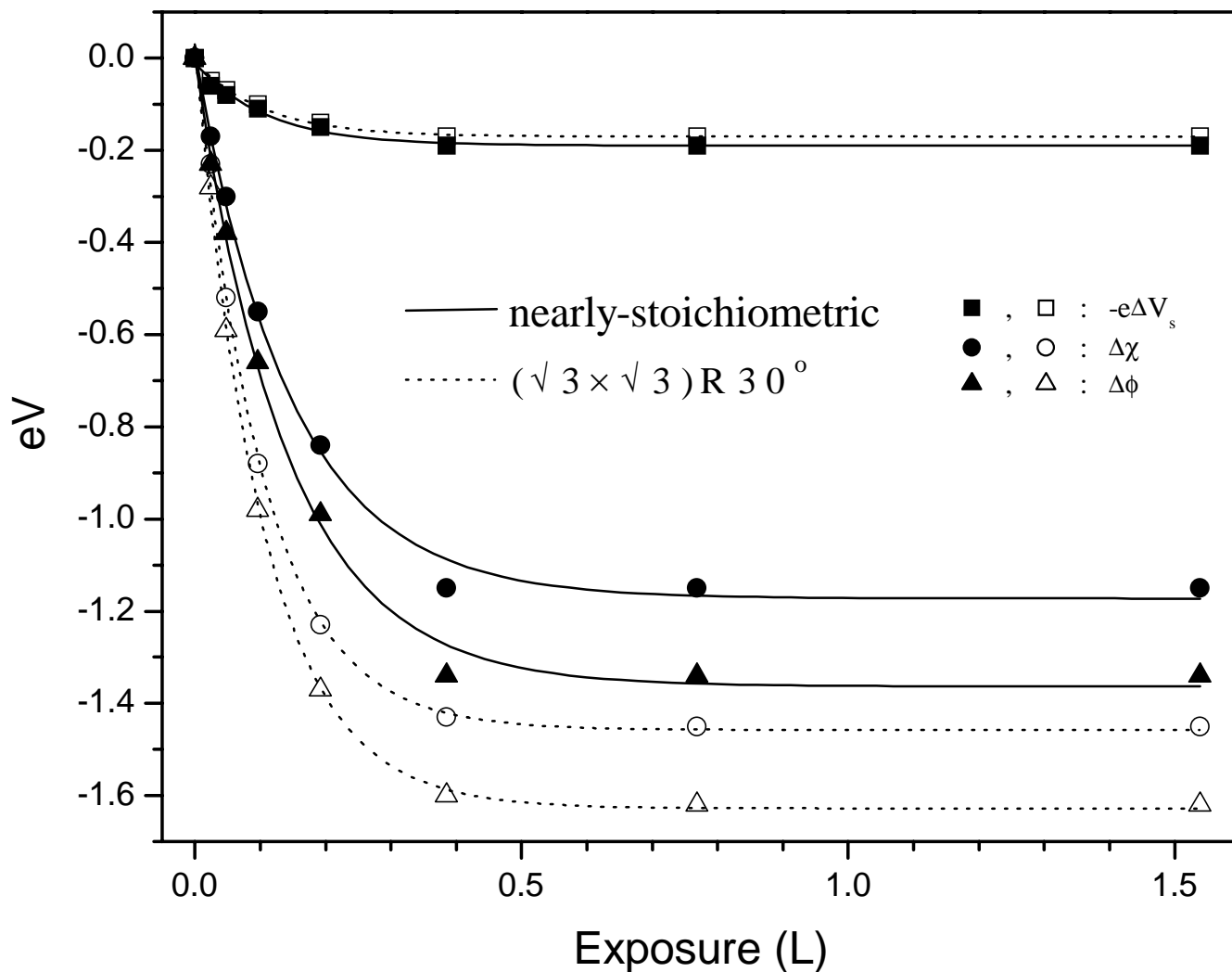


Figure 3.2 He I UPS spectra showing variations in: surface dipole, $\Delta\chi$, band bending, $-e\Delta V_s$, and work function, $\Delta\phi$. All spectra are a function of dose for the nearly-stoichiometric (solid curves) and $(\sqrt{3}\times\sqrt{3})R30^\circ$ (dashed curves) Cu₂O (111) surfaces.

The downward band bending seen on both surfaces gives a direct indication of charge transfer to the surface. At saturation, the maximum downward band bending is 0.18 eV on the nearly-stoichiometric surface and 0.17 eV for the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface.

3.3.2.2 Coverage estimates

Assuming a sticking coefficient of unity for NH_3 up to a dose of 0.4 L allows for an upper-limit estimate of the coverage of 1.9×10^{14} NH_3 molecules/ cm^2 . The number of coordinately unsaturated Cu sites on each surface can be estimated from the unit cell parameters, and the nearly-stoichiometric surface is estimated to expose 3.2×10^{14} singly-coordinate Cu^+ sites/ cm^2 (i.e., one coordinately unsaturated cation per surface unit cell). The number of singly-coordinate Cu^+ cations exposed to the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface is expected to double (6.3×10^{14} Cu^+ sites/ cm^2) with the introduction of one-third of an atomic layer of oxygen vacancies. A fractional coverage is calculated by taking the estimated coverage of NH_3 molecules on the surface and dividing by the total number of Cu cations exposed on the surface. Using the upper-limit coverage estimate for the nearly-stoichiometric surface, a maximum fractional coverage of 0.6 is calculated. Using the upper-limit coverage estimate for the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface, a maximum fractional coverage of 0.3 is calculated. On the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface, the coverage is reduced by half compared to the nearly-stoichiometric surface due to the availability of twice the number of Cu^+ cations, but the NH_3 uptake on the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface is similar to the NH_3 uptake from the nearly-stoichiometric surface. Hence, the absolute coverage is the same on the nearly-stoichiometric and $(\sqrt{3}\times\sqrt{3})R30^\circ$ surfaces even though twice as many Cu^+ cations are available on the $(\sqrt{3}\times\sqrt{3})R30^\circ$ surface. The fractional coverages are

smaller than one might expect because repulsive lateral interactions between NH_3 molecules limit the uptake [9]. Evidence for repulsive interactions is shown in TDS by the decreasing desorption temperatures with increasing NH_3 coverages.

3.3.3 He II UPS

UPS experiments were conducted following a 3.8 L exposure of NH_3 at 125 K. This exposure was sufficient to saturate the surface, as indicated by the He I UPS data. A He II difference curve from the nearly-stoichiometric surface (shown in Figure 3.3) was generated by normalization and alignment to account for band bending of the clean and NH_3 -dosed spectra on substrate features near the valence band maximum. Two NH_3 induced features corresponding to the $1e$ and $3a_1$ MOs of molecular NH_3 are observed in the difference spectra, suggesting primarily a molecular adsorption process. For the nearly-stoichiometric surface, two features corresponding to $1e$ and $3a_1$ MOs of molecular NH_3 appear at binding energies of 5.9 eV and 2.5 eV, respectively (Figure 3.3). Hence, the nearly-stoichiometric surface has a $3a_1$ - $1e$ splitting of 3.4 eV. A similar splitting is observed on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface.

3.4 Discussion

3.4.1 Bonding of NH_3

A chemical bond can generally be considered in terms of ionic and covalent contributions. For the adsorption of NH_3 at a cation site, the ionic contribution can be thought of as an ion-dipole interaction. The covalent interaction can be thought of as Cu $4s$ and $4p$ related bands accepting electron density from the $3a_1$ lone pair orbitals on the

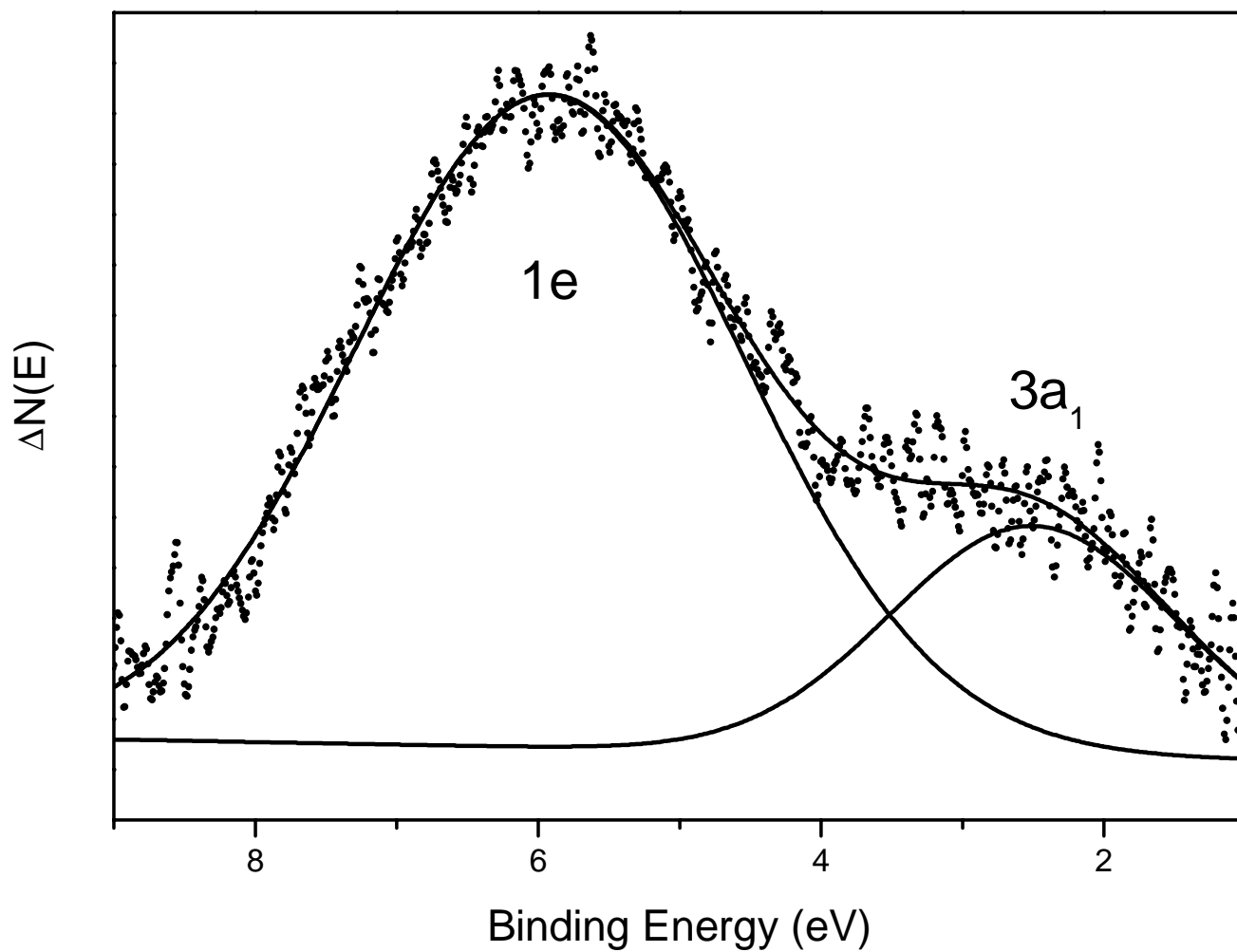


Figure 3.3 He II UPS difference spectra for NH_3 adsorbed at 125 K on the nearly-stoichiometric Cu_2O (111) surface. The $N(E)$ curves are characteristic of molecular NH_3 .

nitrogen atom of NH_3 . The observed changes in electronic properties of Cu_2O and NH_3 upon adsorption give an indication that NH_3 forms covalent bonds to the Cu cations. The downward band bending gives a direct indication of charge transfer to the surface, and the decrease in surface dipole indicates that NH_3 interacts with the Cu^+ cations via the nitrogen lone pair. Two NH_3 induced features corresponding to the $1e$ and $3a_1$ MOs of molecular NH_3 are observed in the He II UPS difference spectra, suggesting primarily a molecular adsorption process. The $1e$ - $3a_1$ splitting for chemisorbed NH_3 is less than the 5.4 eV observed for gas phase NH_3 , indicating a stabilization of the $3a_1$ lone-pair MO upon adsorption on both surfaces [10-11].

NH_3 TDS from Cu_2O (111) is similar to that observed on the Cu (111) surface and NiO (100) films prepared on a Mo (100) support [12,14]. NH_3 TDS from Cu_2O (111) has the same number and progression of desorption features with coverage as NH_3 TDS from Cu (111) but at different desorption temperatures [12]. On Cu (111), two NH_3 desorption features at low coverages in the temperature range from 190 K to 270 K desorb from the first monolayer, and a third NH_3 desorption feature around 170 K desorbs from a bilayer of NH_3 molecules [12,13]. A similar bilayer feature is also seen on NiO (100) at 160 K [14]. Since the nearly-stoichiometric and $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surfaces of Cu_2O (111) expose predominantly singly-coordinate Cu^+ cations, the broad NH_3 TDS feature from 250 K to 500 K (referred to as the α_1 state) and the NH_3 TDS feature at 240 K (referred to as the α_2 state) seen at low coverages are attributed to adsorption of basic NH_3 molecules in the first monolayer at singly-coordinate Cu^+ cations. The NH_3 TDS feature at 160 K (referred to as the β state) is attributed to desorption of second layer NH_3 molecules from the bilayer, similar to the assignment for Cu (111) and NiO (100) [12-14]. Note that the

formation of a γ state corresponding to multilayers, as observed on NiO (100), is not detected since the NH₃ adsorption temperature of 120 K is above the γ -NH₃ (multilayer) desorption temperature of 100-115 K on NiO (100) [14].

NH₃ TDS from Cu₂O (111) has similar desorption temperatures with similar trends in coverage as NH₃ TDS from oriented NiO (100) films [14]. The α_1 state of NH₃ on Cu₂O (111) from 250 K to 500 K is similar in desorption temperature to the α_1 (300-350 K) and α_2 (270 K) states of NH₃ observed on NiO (100), and the α_1 state from Cu₂O (111) decreases in temperature with increasing NH₃ coverages like the α_1 and α_2 states from NiO (100) [14]. The NH₃ molecules in the α_1 and α_2 states on NiO (100) have been attributed to NH₃ molecules bound perpendicular to the surface, where repulsive interactions from parallel dipoles cause the α_1 and α_2 states to decrease in temperature with increased coverage. Similarly, the NH₃ molecules in the α_1 state on Cu₂O (111) are thought to be associated with (nominally) perpendicularly oriented molecules throughout the coverage range of the α_1 state.

The α_2 state of NH₃ on Cu₂O (111) at 240 K is similar in desorption temperature to the α_3 (230 K) state of NH₃ observed on NiO (100), and the α_2 state from Cu₂O (111) seems to remain at the same temperature with increasing NH₃ coverage like the α_3 state from NiO (100) [14]. The NH₃ molecules in the α_3 state on NiO (100) are thought to be associated with tilted molecules with their dipole moments oriented in random directions, lowering the repulsive dipole-dipole interactions between NH₃ molecules in the adlayer. Since the α_2 state on Cu₂O shows the same trend in coverage as the α_3 state on NiO (100), a similar explanation is thought to be applicable to the α_2 state on Cu₂O (111).

3.4.2 Effects of oxygen vacancies

Unlike the case of NH_3 adsorption on SnO_2 (110) surfaces where different cation sites are distinguished in TDS [15], no differences are observed in TDS for NH_3 adsorption on the nearly-stoichiometric and $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ Cu_2O (111) surfaces. The oxygen vacancies on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface expose surface Cu^+ cations presumably with the same coordination number and valence state as the Cu^+ cations on the nearly-stoichiometric surface. In TDS, no new NH_3 desorption features are observed with the introduction of Cu^+ sites around the oxygen vacancies for the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface. Hence, NH_3 molecules must interact with the sites around the oxygen vacancies on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ with either similar or weaker adsorption energies than the Cu^+ cations on the stoichiometric surface. A modification of the TDS spectrum at low temperatures should be noticeable on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface if a significant fraction of the NH_3 molecules interact with Cu^+ sites around the oxygen vacancies with a weaker heat of adsorption. Small amounts of NH_3 interacting with Cu^+ sites around the oxygen vacancies on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface would be difficult to detect in TDS due to an overlap in desorption features. However, given the lack of variation in the desorption traces, the most reasonable explanation seems to be that repulsive forces between the NH_3 molecules limit the uptake at more weakly interacting cation sites associated with oxygen vacancies on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface.

3.4.3 Lewis acidity of Cu cations

In terms of its electronic structure, NH_3 can be thought of as a straight forward probe for Lewis acidity. The $3a_1$ lone pair MO on the nitrogen atom acts as a σ donor. The lowest unoccupied $4a_1$ and $2e$ molecular orbitals lie well above the vacuum level, hence π -backbonding contributions should be negligible [16]. Therefore, NH_3 should be a useful probe molecule of the σ acceptor function of a surface cation. If the strength of the interaction of NH_3 with a cation is taken as a measure of the Lewis acidity of the cation, NH_3 chemisorption indicates that the singly-coordinate Cu^+ cations on the nearly-stoichiometric surface are equal or stronger acid sites than the sites around the oxygen vacancies on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface, since NH_3 either interacts with these sites identically or favors the Cu^+ sites on the nearly-stoichiometric surface.

3.4.4 Propene dissociation

Propene dissociates to a hydrogen and an allyl on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ \text{Cu}_2\text{O}$ (111) surface at low temperature. The recombination of surface allyl and hydrogen for propene desorption is associated with the presence of oxygen vacancies on the surface [5]. Since the sites around the oxygen vacancies on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface are either of equal or less acidity than the Cu^+ sites on the nearly-stoichiometric surface, the dissociation of propene cannot be attributed to an increase in acidity of the sites around the oxygen vacancies on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface. Therefore, it appears that some kind of ensemble effect associated with the local site geometry of Cu^+ cations at the oxygen vacancies on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface facilitates propene dissociation.

3.5 Conclusions

Interactions of NH_3 with the well-defined surfaces of Cu_2O (111) have been investigated using TDS and UPS. NH_3 undergoes reversible molecular adsorption on Cu_2O (111) surfaces at 120 K under UHV conditions with no dissociation observed, and bonds to the surface Cu^+ cations at low coverage via the nitrogen lone pair of the molecules, accompanying a transfer of electrons to the surface Cu^+ cations. Unlike the case of NH_3 adsorption on SnO_2 (110) surfaces where different cation sites can be distinguished in TDS [17], no differences are observed in TDS for NH_3 adsorption on the nearly-stoichiometric and $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ Cu_2O (111) surfaces. The lack of variation seen while using NH_3 as a probe of acidity of Cu^+ cations suggests the sites around the oxygen vacancies on the $(\sqrt{3}\times\sqrt{3})\text{R}30^\circ$ surface are of either equal or less acidity than the Cu^+ sites on the nearly-stoichiometric surface.

3.6 References

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